IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants: J.G. BEDNORZ ET AL.	:	Date: March 29, 1988
Filed: 05/22/87	:	Serial No.: 06/053,307
Group Art Unit: 115	:	Examiner: Dennis Albrecht

FOR: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION TEMPERATURE, AND METHODS FOR THEIR USE AND PREPARATION

RECEIVED 88 APR 19 PM 3:57 GROUP 110

DECLARATION OF RICHARD L. GREENE WITH RESPECT TO HIGH Tc SUPERCONDUCTIVITY

Commissioner of Patents and Trademarks
Washington, D.C. 20231

Sir:

I, Richard L. Greene, hereby declare and say that:

1. I received a Ph.D in physics from Stanford University in 1967, and joined the San Jose, California laboratory of the Research Division of International Business Machines Corp. in 1970. I was the Manager of a group conducting research on organic superconductors and have worked in the field of superconductivity for 20 years. I transferred to IBM Corp. research laboratory in Yorktown, New York, in July 1986, and continued thereafter to conduct research on superconductive materials. From about October 1986 to the present I have worked on high T_c superconducting oxides.

2. At approximately the end of September - first week of October, 1986, my manager, Chang C. Tsuei,showed me a copy of an activity report from the Zurich Research Laboratory of IBM Corporation. This activity report described the work of J.G. Bednorz and K.A. Mueller and their discovery of new superconducting compositions. These materials were mixed copper oxide ceramics that exhibited an onset of superconductivity at a temperature significantly higher than the transition temperatures reported for previously known superconductors. Materials of this general class are now known in the art as high T_c

superconductors. A true copy of this activity report is attached hereto and labeled Exhibit A.

3. Soon after reading this activity report and discussing it with Chang C. Tsuei, I called K.A. Mueller in Zurich and requested samples from him so that I could make measurements on these samples in the United States. This telephone call occurred approximately October 1 - October 6, 1986. My intent was to begin a research project on these materials, as I was very interested in them based on my previous work in superconductivity. My plan at that time was to do experiments which would be complementary to those being conducted by Bednorz and Mueller in Zurich, so that a maximum amount of information could be obtained about these new superconducting materials. Based on the data in this activity report and on the results of susceptibility measurements described to me by Alex Mueller in the aforementioned telephone call, I believed that a new class of superconducting materials with T_c greater than 30K had been discovered.

4. In approximately mid-October, 1986, Praveen Chaudhari, Vice-President, Science, at IBM's Watson Research Laboratory visited the Zurich IBM Lab. Based on my request for samples of the new superconducting material, Chaudhari told me that he had obtained them from Bednorz and Mueller and brought them back to the United States with him. These were about six samples in the Ba-La-Cu-O system. Chaudhari returned to the United States on or about October 20, 1986 and delivered these samples to me. Of these approximately six samples, they varied in the different amounts of La and Ba that were present. Only two of the samples were reported as being single phase materials.

5. Immediately upon receiving these samples, I was in contact with Bednorz and Mueller, via telephone and computer system links, in order to discuss with Bednorz and Mueller the experiments that I would conduct and also to obtain information from Bednorz and Mueller relative to the characteristics of the samples. I had planned to do specific heat measurements of the samples and also resisitivity versus temperature measurements in the presence of a magnetic field. Because of the importance that I attributed to this work, I worked substantially full time on these superconductor materials in order to further characterize them. My first specific heat measurements occurred approximately October 29 and 30, 1986, while I measured resistivity versus temperature in the

presence of a magnetic field in late November, 1986. Continuously throughout the period, October 20, ~~1986 -- February,~~ 1987, I worked on a daily basis to further characterize these materials. At all times, I was in contact with Bednorz and Mueller, exchanged data with them, and worked in close cooperation with them. They provided information to me about the characteristics of the material, as well as providing me up-to-date information concerning the data they had obtained about these materials. A true copy of my computer log from October, 1986 - January 12, 1987 is attached hereto and labeled Exhibit B. Excerpts which do not relate to superconductivity have been deleted. In this exhibit, the identifier for K.A. Mueller is "KAM", while the identifier for J. G. Bednorz is "BED". Bednorz and Mueller are located in Zurich, Switzerland and the computer node for them is ZURLVM1. My identifier is "RGREENE". This computer log details my ongoing computer dialogue with Bednorz and Mueller relative to theirs and my activities on the high T_c superconductor materials. In addition to this computer correspondence, I also talked with Bednorz and Mueller via telephone.

6. During my specific heat measurements of these materials, as well as the measurements of resisitivity versus temperature in the presence of a magnetic field, I was assisted by Albert M. Torressen, who was a laboratory specialist. I also discussed my laboratory experiments with Chang C. Tsuei, S. von Molnar, Merril W. Shafer, Sung Il Park, Thomas Penney, and Arthur R. Williams.

7. The specific details of the apparatus and the data obtained in the specific heat measurements will be described in a separate statement by Albert M. Torressen, the laboratory specialist who worked with me to provide these measurements. Essentially, the specific heat of the apparatus was calculated to provide calibration and background specific heat, after which the sample was introduced into the apparatus and the total specific heat again measured. By subtracting the background specific heat, the specific heat of the superconducting sample is determined. This was done over a temperature range of approximately 2-50K.

8. The specific heat measurements of these superconducting samples were begun approximately October 21, 1986, and were conducted on a daily basis by me and Al Torressen through November and December, 1986.

These specific heat measurements and the curves which were plotted are representative of these superconducting materials, and are also representative of the specific heat versus temperature plots obtained on present samples of superconducting high T_c oxides.

9. In addition to the specific heat measurements described hereinabove and in the accompanying statement of Albert M. Torressen, I also performed measurements of resistivity versus temperature in the presence of a magnetic field, for the samples of Ba-La-Cu-O obtained from Bednorz and Mueller. The specific heat measurements were performed first on these samples, after which I measured resistivity versus temperature in an applied magentic field, in order to further characterize these samples. These resistivity measurements were done at the end of November, 1986, and the beginning of December, 1986. Exhibit C is a true copy of nine pages of my data notebook, together with a copy of the cover of this notebook entitled "Zurich oxide BLCO DATA (T,H)." The date "11/15/86" is also on the cover. Exhibit D is comprised of several pages of plots of resistivity versus temperature for these superconductor samples, as well as resistivity as a function of magnetic field at particular temperatures. In some instances, the RuO_2 sample holder is taken into account into the plots. Generally, these plots represent the graphical expressions of the data contained in Exhibit C. Exhibit E is a composite plot incorporating the different plots found in Exhibit C, and shows resistivity versus temperature for different values of applied magnetic field. I used this composite plot at a seminar that I gave to other researchers at the Yorktown lab on December 12, 1986.

10. In order to obtain the data listed in Exhibit C, I used a laboratory belonging to Stephan von Molnar. Albert M. Torressen, who reported to von Molnar, showed me the necessary equipment to make these measurements, and I preceded to make them on my own. However, many people were aware of these resistivity measurements and viewed the data, including both Thomas Penney and Albert Torressen. In addition, Thomas Penney observed me making these measurements and understood the procedure and nature of my laboratory work.

11. I have numbered the data pages of Exhibit C in red in the upper right hand corner. Page 1 describes the sample set-up that I used for these measurements and the background data in order to ready the

apparatus for the resistivity versus temperature measurements. This sample was the BLCO -21 II, standing for Ba-La-Cu-Oxide material. Page 2 shows two views of the experimental apparatus and the calibration measurements made between particular terminals. The wires A, B, C and F are those which are also shown on page 1.

12. On pages 3, 4, and 5 I had listed the data that applied to the RuO_2 sample holder and the four point probe. The sample was contacted with indium contacts and copper wires were attached to the indium contacts for the measurements. Both DC and AC measurements were made. The resistance of the sample is R_{FC} which was measured at various temperatures with the applied magnetic field H equal to zero (page 4). Pages 5 - 9 show further measurements that were made at different temperature settings and applied magnetic fields. All of the data on these pages were taken by me and entered by me in this notebook.

13. The plot of resistance versus temperature in exhibit D is a plot for the data which was obtained December 3 - December 5, 1986. Referring to Exhibit D, this plot shows the superconducting transition that begins to occur about 35K, where the transition shifts to the left in the presence of a magnetic field. This is an indication of a superconductor.

14. All acts performed by me as described hereinabove occurred in the United States.

15. I further declare that all statements made hereinabove are of my own knowledge and are true and that all statements made on information and belief are believed by me to be true. Further, I declare that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of a Patent Application or any patent issuing thereon.

Richard L. Greene

RICHARD L. GREENE

DATE: 30 March 1988

YO987-074

CC TSUEI EXHIBIT A

Ext. 8237

011 99

9-011-411-724 (Ext.) 8237

IBM

Zurich Research Laboratory
8803 Rüschlikon, Switzerland
Telephone: 01 / 724 81 11
Teleprinter: ITPS CODE ZRL

ACTIVITY REPORT
MAY-JUNE, 1986

August 15, 1986

FOR YOUR	INFO	COMMENTS	FILE

REC'D. SEP 08 1986

PLS	HANDLE		

MATERIAL SCIENCE T. Schneider, Mgr.

SURFACE & MATERIAL SCIENCES E. Courtens, Mgr., Project 4181

Novel Research

Possible High-T_c Superconductivity in the Ba-La-Cu-O System

J.G. Bednorz and K.A. Müller (Project 4196)

We observed a steep decrease of resistivity in sintered Ba-La-Cu-oxide samples, with the highest temperature of the onset in the 35 K range (Fig. 1).

The Ba-La-Cu-O system exhibits a number of oxygen deficient phases with perovskite-like layer-type structures. These are characterized by mixed-valent copper ions (Cu^{2+} and Cu^{3+}) and itinerant electronic states. In addition one expects polaron formation induced by the strong Jahn-Teller effect of Cu^{2+} in an octahedral oxygen environment. Thus our Ba-La-Cu-O system was anticipated to have considerable electron-phonon coupling and metallic conductivity.

Compounds with the composition Ba(x)La(5-x)Cu(5)O(5[3-y]) have been prepared in polycrystalline form. Samples with $x < 0.2$ and $y > 0$, annealed below 900°C under reducing conditions, consist of three phases, one of them a perovskite-like mixed-valent copper compound with K_2NiF_4 type structure. Upon cooling, the samples show a linear decrease in resistivity, then an approximately logarithmic increase, interpreted as a beginning of localization. Finally a steep decrease by up to three orders of magnitude occurs, reminiscent of the onset of percolative superconductivity. The highest onset temperature is observed in the 35 K range. It is markedly reduced by high current densities (Fig. 1). The slow sensitivity decay towards low temperatures might possibly result from 2D superconducting fluctuations of perovskite layers of one of the phases present.

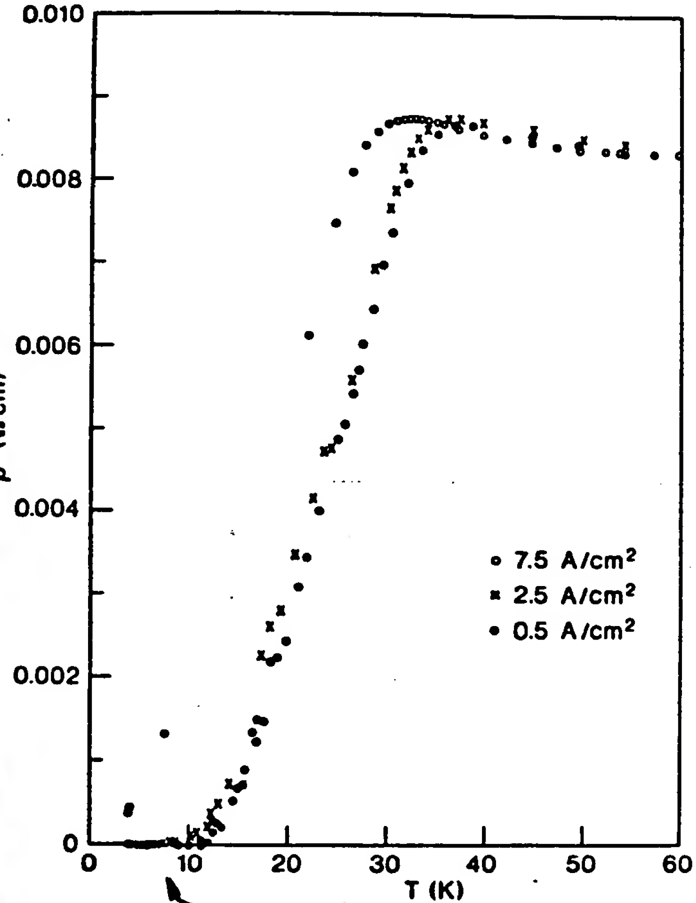


FIG. 1

0.008×10^6 μΩ cm

$\times \frac{1}{1000} = 8$ μΩ cm

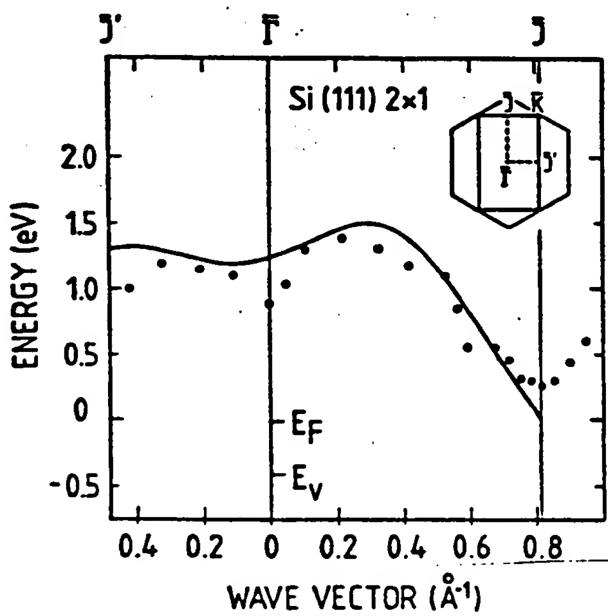


FIG. 2

Z. Phys. B - Condensed Matter 64, 189-193 (1986)

TSUE I
EXHIBIT B

Condensed Matter
Zeitschrift für Physik B

Possible High T_c Superconductivity in the Ba–La–Cu–O System

J.G. Bednorz and K.A. Müller
IBM Zürich Research Laboratory, Rüschlikon, Switzerland

Received April 17, 1986

Metallic, oxygen-deficient compounds in the Ba–La–Cu–O system, with the composition $Ba_xLa_{5-x}Cu_5O_{5(3-y)}$ have been prepared in polycrystalline form. Samples with $x=1$ and 0.75, $y>0$, annealed below 900 °C under reducing conditions, consist of three phases, one of them a perovskite-like mixed-valent copper compound. Upon cooling, the samples show a linear decrease in resistivity, then an approximately logarithmic increase, interpreted as a beginning of localization. Finally an abrupt decrease by up to three orders of magnitude occurs, reminiscent of the onset of percolative superconductivity. The highest onset temperature is observed in the 30 K range. It is markedly reduced by high current densities. Thus, it results partially from the percolative nature, bute possibly also from $2D$ superconducting fluctuations of double perovskite layers of one of the phases present.

I. Introduction

"At the extreme forefront of research in superconductivity is the empirical search for new materials" [1]. Transition-metal alloy compounds of $A15$ (Nb_3Sn) and $B1$ (NbN) structure have so far shown the highest superconducting transition temperatures. Among many $A15$ compounds, careful optimization of Nb–Ge thin films near the stoichiometric composition of Nb_3Ge by Gavalev et al. and Testardi et al. a decade ago allowed them to reach the highest $T_c=23.3$ K reported until now [2, 3]. The heavy Fermion systems with low Fermi energy, newly discovered, are not expected to reach very high T_c's [4].

Only a small number of oxides is known to exhibit superconductivity. High-temperature superconductivity in the Li–Ti–O system with onsets as high as 13.7 K was reported by Johnston et al. [5]. Their x-ray analysis revealed the presence of three different crystallographic phases, one of them, with a spinel structure, showing the high T_c [5]. Other oxides like perovskites exhibit superconductivity despite their small carrier concentrations, n. In Nb-doped $SrTiO_3$, with $n=2\times10^{20}$ cm^{-3}, the plasma edge is below the highest optical phonon, which is therefore unshielded [6]. This large electron-phonon coupling allows a T_c of 0.7 K [7] with Cooper pairing. The occurrence of high electron-phonon coupling in another metallic oxide, also a perovskite, became evident with the discovery of superconductivity in the mixed-valent compound $BaPb_{1-x}Bi_xO_3$ by Sleight et al., also a decade ago [8]. The highest T_c in homogeneous oxygen-deficient mixed crystals is 13 K with a comparatively low concentration of carries $n=2$–4×10^{21} cm^{-3} [9]. Flat electronic bands and a strong breathing mode with a phonon feature near 100 cm^{-1}, whose intensity is proportional to T_c, exist [10]. This last example indicates that within the BCS mechanism, one may find still higher T_c's in perovskite-type or related metallic oxides, if the electron-phonon interactions and the carrier densities at the Fermi level can be enhanced further.

Strong electron-phonon interactions in oxides can occur owing to polaron formation as well as in mixed-valent systems. A superconductivity (metallic) to bipolaronic (insulator) transition phase diagram was proposed theoretically by Chakraverty [11]. A mechanism for polaron formation is the Jahn-Teller effect, as studied by Höck et al. [12]. Isolated Fe^{4+}, Ni^{3+} and Cu^{2+} in octahedral oxygen environment

show strong Jahn-Teller (J.T.) effects [13]. While $SrFe(VI)O_3$ is distorted perovskite insulator, $LaNi(III)O_3$ is a J.T. undistorted metal in which the transfer energy b_π of the J.T. e_g electrons is sufficiently large [14] to quench the J.T. distortion. In analogy to Chakraverty's phase diagram, a J.T.-type polaron formation may therefore be expected at the borderline of the metal-insulator transition in mixed perovskites, a subject on which we have recently carried out a series of investigations [15]. Here, we report on the synthesis and electrical measurements of compounds within the Ba – La – Cu – O system. This system exhibits a number of oxygen-deficient phases with mixed-valent copper constituents [16], i.e., with itinerant electronic states between the non-J.T. Cu^{3+} and the J.T. Cu^{2+} ions, and thus was expected to have considerable electron-phonon coupling and metallic conductivity.

II. Experimental

1. Sample Preparation and Characterization

Samples were prepared by a coprecipitation method from aqueous solutions [17] of Ba-, La- and Cu-nitrate (SPECPURE JMC) in their appropriate ratios. When added to an aqueous solution of oxalic acid as the precipitant, an intimate mixture of the corresponding oxalates was formed. The decomposition of the precipitate and the solid-state reaction were performed by heating at 900 °C for 5 h. The product was pressed into pellets at 4 kbar, and reheated to 900 °C for sintering.

2. X-Ray Analysis

X-ray powder diffractograms (System D 500 SIEMENS) revealed three individual crystallographic phases. Within a range of 10° to 80° (2θ), 17 lines could be identified to correspond to a layer-type perovskite-like phase, related to the K_2NiF_4 structure ($a = 3.79$ Å and $c = 13.21$ Å) [16]. The second phase is most probably a cubic one, whose presence depends on the Ba concentration, as the line intensity decreases for smaller x(Ba). The amount of the third phase (volume fraction > 30% from the x-ray intensities) seems to be independent of the starting composition, and shows thermal stability up to 1,000 °C. For higher temperatures, this phase disappears progressively, giving rise to the formation of an oxygen-deficient perovskite ($La_3Ba_3Cu_6O_{14}$) as described by Michel and Raveau [16].

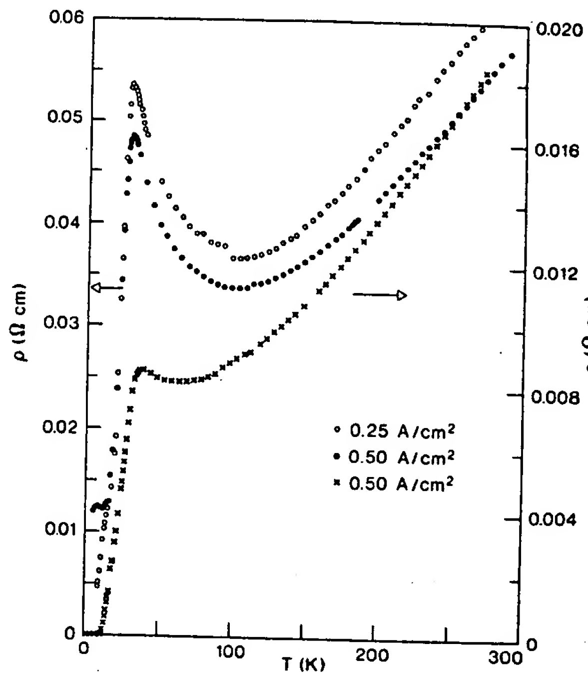


Fig. 1. Temperature dependence of resistivity in $Ba_xLa_{5-x}Cu_5O_{5(3-y)}$ for samples with x(Ba) = 1 (upper curves, left scale) and x(Ba) = 0.75 (lower curve, right scale). The first two cases also show the influence of current density

3. Conductivity Measurements

The dc conductivity was measured by the four-point method. Rectangular-shaped samples, cut from the sintered pellets, were provided with gold electrodes and contacted by In wires. Our measurements between 300 and 4.2 K were performed in a continuous-flow cryostat (Leybold-Hereaus) incorporated in a computer-controlled (IBM-PC) fully-automatic system for temperature variation, data acquisition and processing.

For samples with $x(\text{Ba}) \leq 1.0$, the conductivity measurements, involving typical current densities of 0.5 A/cm², generally exhibit a high-temperature metallic behaviour with an increase in resistivity at low temperatures (Fig. 1). At still lower temperatures, a sharp drop in resistivity (> 90%) occurs, which for higher currents becomes partially suppressed (Fig. 1: upper curves, left scale). This characteristic drop has been studied as a function of annealing conditions, i.e., temperature and O_2 partial pressure (Fig. 2). For samples annealed in air, the transition from itinerant to localized behaviour, as indicated by the minimum in resistivity in the 80 K range, is not very pronounced. Annealing in a slightly reducing atmosphere, however, leads to an increase in resistivity and a more pronounced localization effect. At the same time, the onset of the resistivity drop is shifted

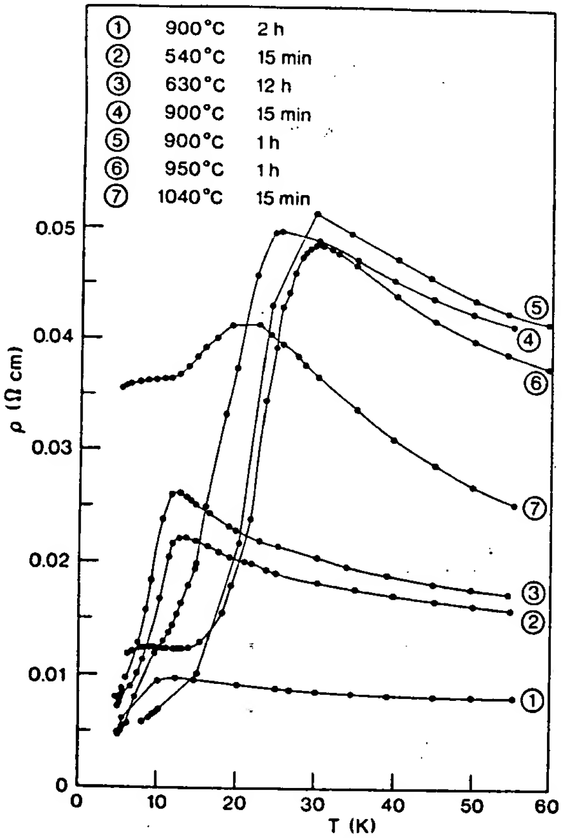


Fig. 2. Low-temperature resistivity of samples with $x(Ba)=1.0$, annealed at O_2 partial pressure of 0.2 bar (curve ①) and 0.2×10^{-4} bar (curves ② to ⑦)

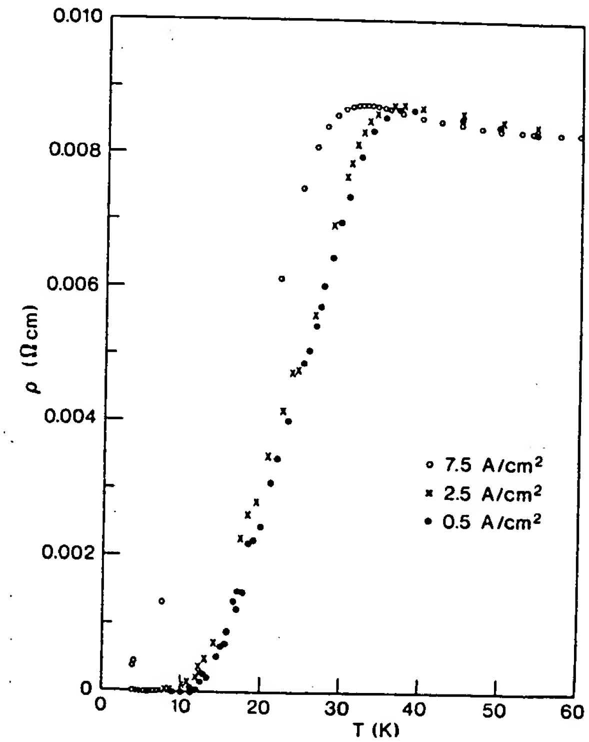


Fig. 3. Low-temperature resistivity of a sample with $x(Ba)=0.75$, recorded for different current densities

towards the 30 K region. Curves ④ and ⑤, recorded for samples treated at 900 °C, show the occurrence of a shoulder at still lower temperature, more pronounced in curve ⑥. At annealing temperatures of 1,040 °C, the highly conducting phase has almost vanished. As mentioned in the Introduction, the mixed-valent state of copper is of importance for electron-phonon coupling. Therefore, the concentration of electrons was varied by the Ba/La ratio. A typical curve for a sample with a lower Ba concentration of 0.75 is shown in Fig. 1 (right scale). Its resistivity decreases by at least three orders of magnitude, giving evidence for the bulk being superconducting below 13 K with an onset around 35 K, as shown in Fig. 3, on an expanded temperature scale. The latter figure also shows the influence of the current density, typical for granular compounds.

III. Discussion

The resistivity behaviour of our samples, Fig. 1, is qualitatively very similar to the one reported in the Li – Ti – O system, and in superconducting $BaPb_{1-x}Bi_xO_3$ polycrystalline thin films [5, 18]. Upon cooling from room temperature, the latter exhibit a nearly linear metallic decrease of $\rho(T)$, then a logarithmic type of increase, before undergoing the transition to superconductivity. One could, of course, speculate that in our samples a metal-to-metal structural phase transition occurs in one of the phases. The shift in the drop in $\rho(T)$ with increasing current density (Fig. 3), however, would be hard to explain with such an assumption, while it supports our interpretation that we observe the onset of superconductivity of percolative nature, as discussed below. In $BaPb_{1-x}Bi_xO_3$, the onset of superconductivity has been taken at the resistivity peak [18]. This assumption appears to be valid in percolative systems, i.e., in the thin films [18] consisting of polycrystals with grain boundaries, or when different crystalline phases with interpenetrating grains are present, as found in the Li – Ti – O [5] or in our Ba – La – Cu – O system. The onset can also be due to fluctuations in the superconducting wave functions. We assume one of the Ba – La – Cu – O phases exhibits this behaviour. Therefore, under the above premises, the peak in $\rho(T)$ at 35 K, observed for an $x(Ba)=0.75$ (Fig. 1), has

to be identified as the start to superconductive cooperative phenomena in the isolated grains. It should be noted that in granular Al, Cooper pairs in coupled grains have been shown to exist already at a point where $\rho(T)$ upon cooling has decreased by only 20% of its highest value. This has been proven qualitatively [19] and more recently also quantitatively [20] by the negative frequency shift occurring in a microwave cavity. In 100 Å films, a shoulder in the frequency shift owing to $2D$ fluctuations was observed above the T_c of the grains. In our Ba – La – Cu – O system, a series of layer-like phases with considerable variety in compositions are known to exist [16, 21], and therefore $2D$ correlations can be present.

The granularity of our system can be justified from the structural information, and more quantitatively from the normal conductivity behaviour. From the former, we know that more than one phase is present and the question arises how large are the grains. This can be inferred from the logarithmic fingerprint in resistivity. Such logarithmic increases are usually associated with beginning of localization. A most recent example is the Anderson transition in granular Sn films [22]. Common for the granular Sn and our samples is also the resistivity at 300 K, lying in the range of 0.06 to 0.02 Ωcm, which is near the microscopic critical resistivity of $\rho_c = 10\ L_0 \hbar/e^2$ for localization. From the latter formula, an interatomic distance L_0 in the range of 100 Å is computed, thus a size of superconducting grains of this order of magnitude must be present. Upon cooling below T_c, Josephson junctions between the grains phase-lock progressively [23] and the bulk resistivity gradually drops to zero by three orders of magnitude, for sample 2 (Fig. 1). At larger current densities, the weaker Josephson junctions switch to normal resistivity, resulting in a temperature shift of the drop, as shown in Fig. 3. The plateau in resistivity occurring below the 80% drop (Fig. 1) for the higher current density of 0.5 A/cm^2, and Fig. 2 curve ⑥) may be ascribed to switching of junctions to the normal state.

The way the samples have been prepared seems to be of crucial importance: Michel et al. [21] obtained a single-phase perovskite by mixing the oxides of La and Cu and $BaCO_3$ in an appropriate ratio and subsequent annealing at 1,000 °C in air. We also applied this annealing condition to one of our samples, obtained by the decomposition of the corresponding oxalates, and found no superconductivity. Thus, the preparation from the oxalates and annealing below 950 °C are necessary to obtain a non-perovskite-type phase with a limited temperature range of stability exhibiting this new behaviour. The formation of this phase at comparatively low temperatures is favoured by the intimate mixture of the components and the high reactivity of the oxalates owing to the evolution of large amounts of H_2O and CO_2 during decomposition.

IV. Conclusion

In the concentration range investigated, compounds of the Ba – La – Cu – O system are metallic at high temperatures, and exhibit a tendency towards localization upon cooling. Samples annealed near 900 °C under reducing conditions show features associated with an onset of granular superconductivity near 30 K. The system consists of three phases, one of them having a metallic perovskite-type layer-like structure. The characterization of the new, apparently superconducting, phase is in progress. An identification of that phase may allow growing of single crystals for studying the Meissner effect, and collecting specific-heat data to prove the presence of high T_c bulk superconductivity. //

The authors would like to thank H.E. Weibel for his help in getting familiar with the conductivity measurement system, E. Courtens and H. Thomas for discussions and a critical reading of the manuscript.

References

1. Tinkham, M., Beasley, M.R., Larbalestier, D.C., Clark, A.F., Finnemore, D.K.: Workshop on Problems in Superconductivity, Copper Mountain, Colorado, August 1983, p. 12
2. Beasley, M.R., Geballe, T.H.: Phys. Today 36 (10), 60 (1984)
3. Müller, J.: Rep. Prog. Phys. 43, 663 (1980)
4. Ott, H.R.: Unconventional Superconductivity. Zürich Phys. Soc. Seminar, Zürich, February 13, 1986
5. Johnston, D.C., Prakash, H., Zachariasen, W.H., Viswanathan, R.: Mat. Res. Bull. 8, 777 (1973)
6. Baratoff, A., Binnig, G.: Physics 108 B, 1335 (1981)
Baratoff, A., Binnig, G., Bednorz, J.G., Gervais, F., Servoin, J.L.: In: Superconductivity in *d*- and *f*-Band Metals, Proceedings IV Conference in 'Superconductivity in *d*- and *f*-Band Metals'. Buckel, W. and Weber, W. (eds), p. 419, Kernforschungszentrum Karlsruhe 1982
7. Binnig, G., Baratoff A., Hönig, H.E., Bednorz, J.G.: Phys. Rev. Lett. 45, 1352 (1980)
8. Sleight, A.W., Gillson, J.L., Bierstedt, F.E.: Solid State Commun. 17, 27 (1975)
Batlogg, B.: Physica 126 B, 275 (1984)
9. Thanh, T.D., Koma, A., Tanaka, S.: Appl. Phys. 22, 205 (1980)
10. Mattheis, F., Hamann, D.R.: Phys. Rev. B 26, 2682 (1982); *ibid.* 28, 4227 (1983)
11. Chakraverty, B.K.: J. Phys. Lett. 40, L99 (1979); J. Phys. 42, 1351 (1981)
12. Höck, K.-H., Nickisch, H., Thomas, H.: Helv. Phys. Acta 56, 237 (1983)
13. Englmann, R.: In: The Jahn-Teller Effect in Molecules and Crystals. London, New York: Wiley Interscience 1972
14. Goodenough, J.B., Longo, M.: Magnetic and other properties of oxide and related compounds. In: Landolt-Boernstein New

Series. Vol III/4a: Crystal and solid state physics. Hellwege, K.H., Hellwege, A.M. (eds.), p. 262, Fig. 73. Berlin, Heidelberg, New York: Springer-Verlag 1970
15. Bednorz, J.G., Müller, K.A.: (in preparation)
16. Michel, C., Raveau, B.: Chim. Min. 21, 407 (1984)
17. Bednorz, J.G., Müller, K.A., Arend, H., Gränicher, H.: Mat. Res. Bull. 18 (2), 181 (1983)
18. Suzuki, M., Murakami, T., Inamura, T.: Shinku 24, 67 (1981) (in Japanese)
Enomoto, Y., Suzuki, M., Murakami, T., Inukai, T., Inamura, T.: Jpn. J. Appl. Phys. 20, L661 (1981)
19. Müller, K.A., Pomerantz, M., Knoedler, C.M., Abraham, D.: Phys. Rev. Lett. 45, 832 (1980)
20. Stocker, E., Buttat, J.: Solid State Commun. 53, 915 (1985)
21. Michel, C., Er-Rakho, L., Raveau, B.: Mat. Res. Bull. 20, 667 (1985)
22. Van Haesendonck, C., Bruynseraede, Y.: Phys. Rev. B 33, 1684 (1986)
23. Deutscher, G., Entin-Wohlman, O., Fishman, S., Shapira, Y.: Phys. Rev. B 21, 5041 (1980)

J.G. Bednorz
K.A. Müller
IBM Zürich Research Laboratory
Säumerstrasse 4
CH-8803 Rüschlikon
Switzerland

Note Added in Proof

Chemical analysis of the bulk composition of our samples revealed a deviation from the ideal La/Ba ratios of 4 and 5.66. The actual ratios are 16 and 18, respectively. This is in agreement with an identification of the third phase as CuO.

June 1985 -

VII

TSUEI
EXHIBIT C

university note book

NAME W. Kateley + C.C. Tsuei

SUBJECT Low temp. T.C.

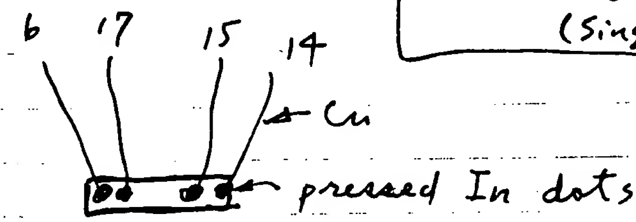
VERNON McMILLAN Inc.
THE ROYAL LINE

No. 06-9504 (S-1870-CM) · 11 IN. x 8½ IN. (28 cm x 21.6 cm) · 50 SHEETS · COLLEGE & MARGIN RULED

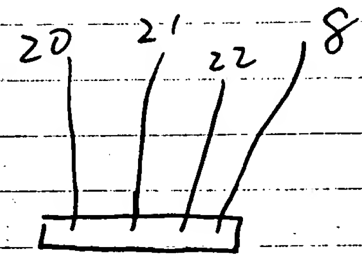
VERNON McMILLAN, Inc., ELIZABETH, N.J. 07208

BLCO 21 – II
Zurich Oxide oct, '86
(Single phase ?)

A2
#4



B2
#5



BLCO 2
I
10/22/86

dewar pumped to
3×10^{-5} Torr 11/9/86

Ext. 8237

GREENE EXHIBIT A

011 99

MAR 23 APR 4 1986 PAT. & TRADE MARK OFFICE

IBM

Zurich Research Laboratory
8803 Rüschlikon, Switzerland
Telephone: 01 / 724 81 11
Teleprinter: ITPS CODE ZRL

9 – 011 – 411 – 724 (Ext.) 8237

ACTIVITY REPORT
MAY-JUNE, 1986

August 15, 1986

FOR YOUR	INFO	COMMENTS	FILE

REC'D. SEP 08 1986

PLS	HANDLE		RI	

MATERIAL SCIENCE T. Schneider, Mgr.

SURFACE & MATERIAL SCIENCES E. Courtens, Mgr., Project 4181

Novel Research

Possible High-T_c Superconductivity in the Ba-La-Cu-O System

J.G. Bednorz and K.A. Müller (Project 4196)

We observed a steep decrease of resistivity in sintered Ba-La-Cu-oxide samples, with the highest temperature of the onset in the 35 K range (Fig. 1).

The Ba-La-Cu-O system exhibits a number of oxygen deficient phases with perovskite-like layer-type structures. These are characterized by mixed-valent copper ions (Cu^{2+} and Cu^{3+}) and itinerant electronic states. In addition one expects polaron formation induced by the strong Jahn-Teller effect of Cu^{2+} in an octahedral oxygen environment. Thus our Ba-La-Cu-O system was anticipated to have considerable electron-phonon coupling and metallic conductivity.

Compounds with the composition Ba(x)La(5-x)Cu(5)O(5[3-y]) have been prepared in polycrystalline form. Samples with $x < 0.2$ and $y > 0$, annealed below 900°C under reducing conditions, consist of three phases, one of them a perovskite-like mixed-valent copper compound with K_2NiF_4 type structure. Upon cooling, the samples show a linear decrease in resistivity, then an approximately logarithmic increase, interpreted as a beginning of localization. Finally a steep decrease by up to three orders of magnitude occurs, reminiscent of the onset of percolative superconductivity. The highest onset temperature is observed in the 35 K range. It is markedly reduced by high current densities (Fig. 1). The slow sensitivity decay towards low temperatures might possibly result from 2D superconducting fluctuations of perovskite layers of one of the phases present.

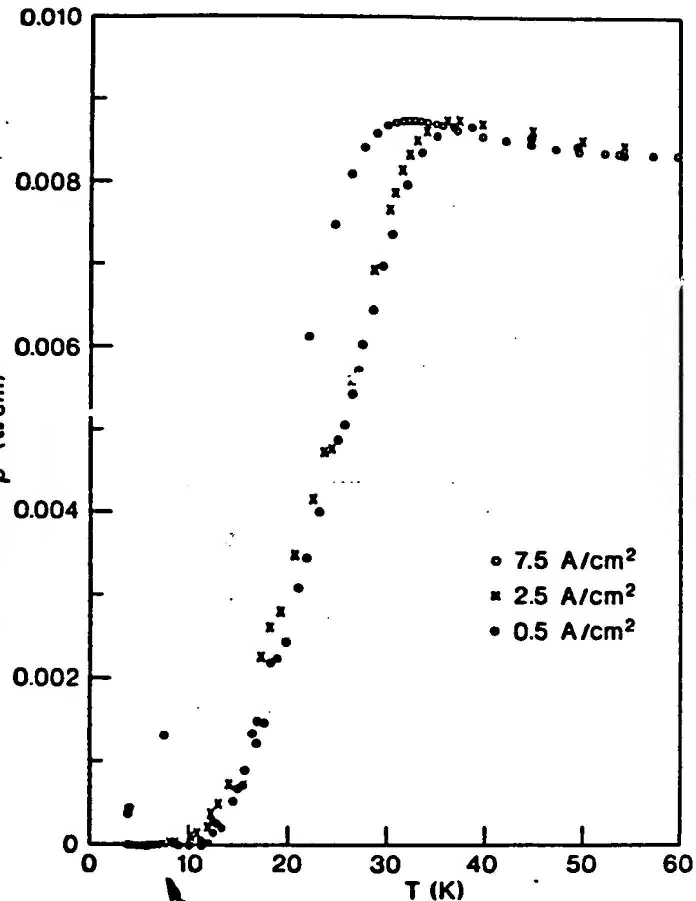


FIG. 1

0.008×10^{6} μΩ cm

$\times \frac{1}{1000} = 8$ μΩ cm

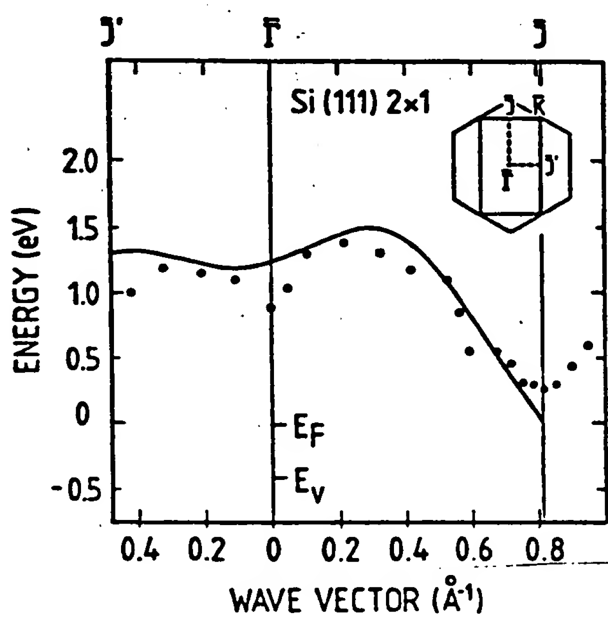


FIG. 2

GREENE EXHIBIT B

Date: 6 October 1986, 15:37:18 EDT From: RGREENE at YKTVMZ To: KAM at ZURLVM1

Alex;

Have you made any decision on my proposed specific heat experiment? I am anxious to try it. I think I can do it rather quickly after getting some samples. It may be difficult to see the transition near 30K because of a large phonon background but at the very least we could get a good estimate of the electron density of states and the Debye phonon contribution. Once I have a good specific heat between 2K and 40K I can make a better effort to resolve the electronic effect at Tc if it is small....I think I can see a 1% effect if the transition is not too smeared in temperature. Perhaps you would like to come to Yorktown and work with me on this experiment? Let me know. Best regards.

Rick

P.S. This is a good time for me to do some experiments on your exciting new compound since I am not heavily involved in other projects yet. I could get access to tunneling and neutron scattering equipment which would be very useful for seeing which phonons (if any) are involved in causing such a high Tc.

Date: 14 October 1986, 10:42:19 EDT From: RGREENE at YKTVMZ To: KAM at ZURLVM1

Hi Alex:

This note is to give you my user id and node on the VM system. You can see them above. When you send the samples for the specific heat experiment let me know via VM. My office at Yorktowm is 02-026. I will make the specific heat my highest priority and should be able to start the experiment as soon as the samples arrive. I will keep you informed on the progress of the experiment.....it will probably take a few weeks to get reliable data assuming there are no unexpected problems.

As I said on the telephone you can ignore the sample dimensions sent to you by my manager C. Tsuei. He did not talk to me before sending you his VM note and he did not understand the requirements of the specific heat apparatus. What I need are samples to cover an area of 2mm x 2mm on the bolometer. Some extra samples will also be necessary in case we break or lose the primary samples. It would be best to not compress the samples or bind them together with any foreign materials which could alter the specific heat.

Best Regards,

Rick

Date: 15 October 1986, 15:02:34 EDT From: RGREENE at YKTVMZ To: SANDRO

Sandro; I have a court at 5pm. Do you want to play?

Rick

Date: 16 October 1986, 09:06:42 EDT From: RGREENE at YKTVMZ To: GGRIN

I'm thinking about taking my son to Mohansic tomorrow afternoon around 1:30. If you want to join us let me know.

Rick

Date: 16 October 1986, 13:27:32 EDT From: RGREENE at YKTVMZ To: JBMART

The reference is PRL 57, 1177(1986). I think a pressure experiment might be interesting. Let me call Chaikin and Brian first then I'll get back to you.

Rick

[illegible]

Greene

Date: 20 October 1986, 08:51:36 EDT From: RGREENE at YKTVMZ To: LOUGHRAN at ALMVMC

Hi Diane;

Starting to get cold around here but at least the sun is shining. Hope all is well with you. You can discard the Chaikin-Greene manuscript. It's been published and I have the reprints. Thanks for forwarding any remaining mail that comes to Almaden.....it takes a long time for scientific types to know when one has moved. I'll be seeing you in Jan.

Regards,

Rick

Date: 20 October 1986, 15:18:13 EDT From: RGREENE at YKTVMZ To: KAM at ZURLVM1

Alex;

The samples have arrived. They are bigger than I expected and all appear to be compressed pellets. Before I start on the specific heat I need to know a few things.

1.What is the difference between the samples marked I(red) and II(black)?

2.Have the samples been compressed with any foreign material, such as a binder?

3.Can the samples be cut without falling apart? If so do you recommend using a string saw or a razor blade or something else? Will water damage them?

? D.J. R.G know how samples were made

4.Has the magnetic susceptibility been measured on any of these samples or on other samples from the same batch? I may want to measure the resistivity or susceptibility on these particular samples to make sure they exhibit the behavior you found before spending a big effort on the specific heat.

We are measuring the background specific heat of our apparatus up to 40K tomorrow...hopefully by the end of the week we will begin your samples so please call or send me via VM the answers to the above questions as soon as possible.

Best regards,
Rick

Rick

Date: 23 October,1986, 13:43:17 EDT From: RGREENE at YKTVMZ To: BED at ZURLVM1 cc: KAM at ZURLVM1

Hi George , Alex;

Just a note to keep you informed of our progress. We are almost finished with the background specific heat. Tomorrow we will mount a 25mg slice of your sample BLCO2....it should take about a week to get the data in the earth's magnetic field. It probably will be necessary to also measure the specific heat in a magnetic field to accurately determine the superconducting contribution. Do you have any data on the critical field for this sample...if not we can measure it ourselves. Also I need to know if the samples you sent me are each a single phase.....from your x-ray studies. I haven't received your preprint yet....perhaps some of my questions are answered there.

I will be away from the lab tomorrow and look forward to your response on Monday. Best regards.

Rick

Date: 23 October 1986, 14:00:11 EDT From: RGREENE at YKTVMZ To: MALOZEM

Alex;

Sorry I haven't gotten back to you but I have been very busy with two exciting experiments.....the specific heat of the new Zurich high

temperature superconductor and the 2D melting X-ray experiment with Paul which finally looks like it will work. I'm not really sure if there are any easily defined X-ray experiments that can be done to prove or disprove the nice model you presented this morning but I will think more about this. However given my present experimental committments it will be a few months before I could realistically do anything.Keep me informed. Thanks.

Rick

Date: 23 October 1986, 14:27:22 EDT From: RGREENE at YKTVMZ To: BED at ZURLVM1

George; Thanks for the Susceptibility info. I'm glad that I chose BLCO2 I for the first experiment.How wide in temperature is the para-diamagnetic transition in this sample? Regards.

Rick

Date: 23 October 1986, 18:58:35 SET From: j.g.bednorz BED at ZURLVM1 To: RGREENE at YKTVMZ

Hi Rick

Here are the results of our susceptibility measurements, done on the samples You got from me. I'll give You the temperatures where the para- to diamagnetic transition occurs.

BLCO2 I 32K	BLCO2 II 26-27K
BLCO8 I 13-14K	BLCO8 II 25-26K
BLCO21I 25K	BLCO21II 27-28K

So You don't need to involve somebody else with these measurements, which I prefere doing myself here.
While typing this, I got the message that You send a note.

Salu
George.

Date: 23 October 1986, 16:00:52 EDT From: RGREENE at YKTVMZ To: TFHEINZ

Tony;
I can't serve on the colloquim committee this year. I'll try to think of possible speakers however. Sorry and thanks for thinking of me.

Rick

Date: 23 October 1986, 17:32:09 EDT From: RGREENE at YKTVMZ To: GRANT at ALMVMC

Hi Grant;
Where have you been hiding? I need to talk to you since you didn't answer my last note. I'll be here on Monday..try me then.

the old boss

YKTVMZ To: VERMLI

at Yorktown. Thanks and regards.

Rick

Date: 27 October 1986, 08:32:34 EST From: RGREENE at YKTVMZ To: GGRIN

Got your note too late.....sorry I missed the big game. Let's try the ... I won't have time for a real golf game for a

Date: 28 October 1986, 17:30:52 EST From: RGREENE at YKTVMZ To: BED at ZURLVM1, KAM at ZURLVM1

Hi George, Alex:

Did you get the last two notes that I sent you? I'm measuring BLCO2 this week...nothing definitive yet. I'll keep you informed. What is the critical field of this sample? Is BLCO2-I all the same phase? I haven't received your preprint yet...have you sent it? Best regards.

Rick

Date: 29 October 1986, 17:20:53 EST From: RGREENE at YKTVMZ To: GGRIN

Hey Rod;

Date: 29 October 1986, 16:41:22 SET From: j.g.bednorz BED at ZURLVM1 To: RGREENE at YKTVMZ

Hi Rick,
Sorry for letting you wait so long to get an answer. Alex told me that he sent the reprint already 10 days ago. I have sent you a second one today, in case the letter got lost somewhere.

Concerning your questions:
From our measurements we can tell you that the critical field Hc2 is higher than 1.5 kG.

Now about the phases present in our samples:

```
BLC02 I   3 phases: °cub. perovskite/tetrag. perovskite/CuO
BLC02 II  2 phases:       "        /         "        /---
BLC08 I   2 phases:       "        /         "        /---
BLC08 II  1 phase :  ----------/             "        /---
BLC021I   2 phases:       "                  "        /---
BLC021II  1 phase :  ----------/             "        /---
```

Best regards also from Alex

George.

Date: 30 October 1986, 09:20:04 EST From: RGREENE at YKTVMZ To: GRANT at ALMVMC

Hi Grantie;

I'm here ..where are you? Don't even have a phone answer any more. How come you didn't answer the questions in my last note.

As for the 3M meeting I am suposssed to share a room with Torrance starting Sunday nite. I'm not sure if he's still coming or how long he's staying. Check with him and you can share the room with us or replace him. Let me know.

Greene

Date: 30 October 1986, 09:31:20 EST From: RGREENE at YKTVMZ To: BED at ZURLVM1, KAM at ZURLVM1

Hi Alex and George:

I just tried to reach you by telephone without success so here is a note. We have measured the specific heat(C) of BLC02-I from 2-40K...the analysis is not yet complete but the prliminary data does not show any bump in C near or below 32K. However at this stage we could only see a bump or jump if it was greater than 10% of C so more accurate ex-

periments will be required.Since BLCO2-I is a 3 phase sample it was not a good choice for the measurement since I will not be able to analyze the data for density of states and Debye Temp. Do you know how much of each phase is present in this sample? Also is the cubic perovskite a metal or insulator?

It would be better if you had some single phase single crystals of the tetragonal phase. Is this possible? We could measure samples as small as a few milligrams.

Without crystals I am planning to measure BLCO8-II next since this is a single phase. Once you send me the info on the chemical composition and structure of this phase I can analyze the data and hopefully get results that we can publish.The measurements will take another week if all goes well. If we have to put on a magnetic field this will take several more weeks... specific heat data is tedious to obtain and analyze even with a computer.

Please answer the above questions as soon as possible. I am still waiting for your preprint...the first one must have gotten lost. Did you send it by external mail? Best regards.

Rick

Date: 30 October 1986, 18:30:43 SET From: j.g.bednorz BED at ZURLVM1 To: RGREENE at YKTVMZ

Hi Rick,

BLCO21II or BLCO8II would be good to try.

BLCO21II shows a more pronounced resistivity drop, as compared to the sample I. BLCO8II I could not check till now.

The composition is Ba0.15 La1.85CuO4-x and Ba0.10La1.90CuO4-x respectively.The structure of La2CuO4 is a layered perovskite of K2NiF4 type.

The pure material is orthorhombically distorted. Exchanging La by Ba is leading, as we belief, to the formation of a tetragonal unit cell.

Our powder diffraction pattern can be indexed with a bodycentered lattice and a=3.79A and c=13.21A for xBa around 0.1. For crystals with xBa=0.02 I also checked the lattice parameters by single crystal precession experiments. But here we aready have the problem. These crystals have been obtained from powders with xBa=0.1, so we have to expect seggregation and it will take a while, to get the crystals with a composition where the resistivity drop is observed in the powders.

To your question about the cubic perovskite,it shows metallic conductivity as well.

I really hope, that you get the preprint very soon.

Best regards George.

Date: 30 October 1986, 15:06:11 EST From: RGREENE at YKTVMZ To: BED at ZURLVM1

George; Thanks for your quick answer to my questions. I forgot to ask you if you know the relative weight % of the 3 phases in sample BLCO2-I. If so I may still be able to get some useful information from the data we have taken so far.

I also just realized that you could send me the preprint via VM assuming it was typed on line. Please see if your secretary can do this. Thanks and regards.

Rick

Date: 3 November 1986, 16:58:28 EST From: RGREENE at YKTVMZ To: JERRYT at ALMVMC

Hi Jerry;

All is set for our room at the Hyatt starting Sunday nite the 16th. I'm not sure when I'll arrive but they have your name attached to the room also and it's guaranteed for late arrival. See you there. I saw some article recently about an organic ferromagnet....I think in JETP letters. Do you know about that work?

Rick

Date: 4 November 1986, 17:00:53 EST From: RGREENE at YKTVMZ To: SANDRO

I cannot play tomorrow...sorry.Next week.If I can change my schedule tomorrow I will call you in the morning.

Rick

Date: 11 November 1986, 10:04:02 EST From: RGREENE at YKTVMZ To: BED at ZURLVM1

Hi George;

No I have not given up...in fact I just tried to reach you by phone.My terminal is not working since I just changed my office so It may take me a little longer to respond to messages.

At any rate I have finished the specific heat measurement from 4-35K in zero magnetic field. It will take a few days to finish the data analysis but there is no obvious bump in the specific heat indicating superconductivity. This is not really too surprising given the very broad transition you have found in resistivity and susceptibility.

I expect to get some useful information from the data anyway but for this I need the exact composition of BLCO21-II.Is it Ba.15La1.85CuO(4-.15)? Please send this as soon as possible by VNET....I will get back to you and ALex later with more info. Regards.

Rick

Date: 12 November 1986, 09:19:56 EST From: RGREENE at YKTVMZ To: GRANT at ALMVMC

Greene

Date: 13 November 1986, 13:54:49 EST From: RGREENE at YKTVMZ To: MALOZEM

Alex;

I'll be happy to talk about the prospects of using magnetic X-ray scattering for thin films and interfaces. It will only be a summary of what has been done and my thoughts on what else could be done. The rest of your proposed program looks great. It's a good idea to have such an internal meeting.

Rick

Date: 14 November 1986, 10:17:09 EST From: RGREENE at YKTVMZ To: BED at ZURLVM1, KAM at ZURLVM1

Hi Alex and George;

I will be away from the lab until 24 Nov. so I thought I would let you know the present status of the specific heat (SH) experiment and my future plans.

So far we have measured BLCO21 from 3-35K.There is no evidence for a bump in SH anywhere....to a 5% accuracy. I have analyzed in detail the data between 3-10K. Here the SH is linear on a C/T vs T2 plot. The intercept gives a value for gamma of 5.9 mj/mole-K2. This is a rather large value compared to other metals and suggests that most of the BLCO21 sample is in the normal state. However to be sure of this we must measure the sample in a magnetic field large enough to suppress the superconductivity. This we will start while I am away. Also we must run a test sample such as copper or silicon to know the accuracy of our gamma determination. All this will take 2-3 more weeks. As you see it takes considerable effort to do a reliable specific heat measurement which makes it very important that we have well characterized, single phase samples. As we discussed yesterday George it may be better to do the SH experiment on a bunch of single crystals if you can prepare them.Five mg of material should be enough to get reliable data.

We will also measure the critical field up to 9T via resistivity. I want to do this first so I have some idea of the field necessary to get the normal state at 3K....our SH apparatus has a field of 5T maximum.

I'll talk with you when I return. I am still quite excited about these new materials and hope that we can continue to collaborate on various experiments even if the specific heat does not give evidence for bulk superconductivity. I should remind you that it took many years of work before the BaPbBi Oxides were shown to be bulk Superconductors.

Best regards,
Rick

Date: 25 November 1986, 09:43:48 EST From: RGREENE at YKTVMZ To: PARKIN at ALMVMC

Hi Stuart;

Thanks for your note. I haven't heard from Helmut but he is probably very busy starting his new job. Haven't heard about the Japan proceedings either.....are you still interested in organic metals? What is happening with your work on thin films? I expect to be out to San Jose sometime in January and you can bring me up to date.

Until then I am very busy with X-ray scattering and some other experiments on new inorganic materials. Have a good holiday season.

Best regards

Rick

Date: 25 November 1986, 10:35:50 EST From: RGREENE at YKTVMZ To: BED at ZURLVM1, KAM at ZURLVM1

Hi Alex and George;

I have returned from my trip and will once again start work on your new superconductor. This week is the Thanksgiving holiday so not much will happen until next week. The specific heat apparatus is now modified to make measurements in a magnetic field....however we must first calibrate and check that it works with some known material.

Please tell me what is happening with your studies of time dependent effects. Is the sample BLCO21 still good....we have not yet measured the resistivity in a field as a function of T but we plan to along with the specifi c heat experiment.Perhaps you should send me some new single crystals for the next experiment.....I don't want to waste time on a bad sample.

I would like to send an abstract to the March APS meeting on the specific heat results. Is this agreeable with you? The abstracts are due the end of next week (Dec.5) so let me know soon. At this stage there is not much definitive to say but I can still write a general abstract about specific heat and I'm sure I will have definitive results by the time of the meeting.

Best Regards,

Rick

Date: 26 November 1986, 09:56:43 EST From: RGREENE at YKTVMZ To: KAM at ZURLVM1

Hi Alex;

Are you sending your susceptibility preprint to people outside of IBM? If so Ted Geballe at Stanford would like a copy...he saw your paper in Z.Physic and called me to see if I knew about your work.

I can send him a copy if you are agreeable. Please let me know about this and more importantly the answer to my note of yesterday.

Best regards,

DOI 13

Date: 1 December 1986, 17:31:01 EST From: RGREENE at YKTVMZ To: KAM at ZURLVM1, BED at ZURLVM1

Hi Alex and George:

Here is a draft of the abstract that I would propose submitting to the APS March meeting. Please make any changes or comments and let me know today. I look at this as a way to publisize your work in the USA and to present whatever specific heat results are obtained by March.

POSSIBLE HIGH Tc SUPERCONDUCTIVITY IN THE Ba-La-Cu-O SYSTEM

We report measurements on new oxide superconductors of the composition La(2-x)Ba(x)CuO(4-y) with x<<1 and y>0. Polycrystalline samples with x=.15 show a resistivity drop of three orders of magnitude and a transition from Pauli paramagnetism to diamagnetism with an onset temperature between 30-35K. (ref 1 and 2....your two papers). The transition is complete by 10K and magnetic field studies suggest superconductivity of a percolative or granular nature. Our specific heat experiments indicate a large electron density of states but no evidence of a sharp jump near Tc---consistent with the small Meissner signal observed (2% of complete flux expulsion) and the broad transition width. These measurements, along with X-ray and critical field results, will be analyzed for the possibility of high Tc superconductivity in these new oxide materials.

The authors would be the three of us and Steve VonMolnar (whose apparatus I am using)....possibly I would add Al Torresen (Steve's assistant) without whom the specific heat experiments could not have been done.

The abstract could perhaps be a bit longer but there may not be much space after the authors and references are included.

Regards,
Rick

Date: 2 December 1986, 09:17:12 EST From: RGREENE at YKTVMZ To: KAM at ZURLVM1

Alex;
I scheduled your seminar for 8 Jan at 3:30pm....this was the only time I could get a room. Please send me a title and short abstract so I can get it on the lab calender as soon as possible. Do you need a hotel reservation? Regards.
Rick

P.S. Plan on saving some time on 9 Jan. to discuss our specific heat data.If you would like to go out together for dinner on the 8th let me know.

Date: 4 December 1986, 10:48:02 EST From: RGREENE at YKTVMZ To: BED at ZURLVM1

Hi George;
I just tried to telephone you. I am measuring the resistance and critical field of sample BLCO-21. So far it reproduces the data in your Z. Physik paper...I don't see a bump except perhaps near 25K (but I need to take more points). The surprising thing is that a small field (1000 Oe) increases the Resistance to the value at 25K but at higher fields (up to 7Tesla) there is almost no more change in R. Tell you more when I have more data.....so far it suggests that doing the specific heat in low field will be useful.

Would you please send me whatever info you have on the structure of the superconducting phase i.e. a picture and a powder X-ray that gives the Bragg peak positions.
What have you learned about the time changes in these samples? I would like some fresh single phase samples for our next specific heat experiment...to begin at the end of next week. If you have single crystals that would even be better....but I realize this is a difficult problem.

Regards,

Rick

Date: 5 December 1986, 10:56:34 EST From: RGREENE at YKTVMZ To: ORR

OK. What are you up to? Dropin and see me sometime in vonMolnars lab.

Rick

Date: 5 December 1986, 11:10:42 EST From: RGREENE at YKTVMZ To: KAM at ZURLVM1, BED at ZURLVM1

Hi Alex and George:

I'm getting some good critical field results now although I still don't totally trust my contacts. The resistance vs. temp. follows your data but there seems to be two superconducting regions (perhaps 2 phases).. one below 22K and the other below 33K. The critical fields are very different in these two temperature ranges. The good news is that I am getting a critical field vs temp curve between 20-30K and this will alllow me to estimate gamma to compare with the specific heat gamma. Incidently the critical field at 4K is greater than 7Tesla (as expected for a high Tc material) so we may eventually want to go to the MIT magnet lab to measure it better.

The specific heat exp. is progressing nicely and we will be finished with all our calibrations next week. What sample do you recommend that I use based on your recent work?

As soon as I have collected and plotted all the critical field data I will send you a figure along with the abstract to the March meeting.

Best regards,

Rick

P.S. Please send me whatever info you have on the structure of the SC phases.

I am giving an internal journal club seminar on your resistivity and susceptibility papers.

Date: 8 December 1986, 09:26:48 EST From: RGREENE at YKTVMZ To: LOUGHRAN at ALMVMC

happy holidays....see you in Jan (maybe)

Rick

Date: 3 December 1986, 16:39:02 SET From: KAM at ZURLVM1 To: RGREENE at YKTVMZ

Rick,here is the title and abstract for my seminar :

'Superconducting and Structural Properties of the BaLaCuO System'

Resistivity and susceptibility measurements as well as x-ray powder analysis carried out at the Rueschlikon laboratory will be described.The electric and magnetic data indicate the existence of a percolative superconductor with onset above 30 K.The newest magnetisation measurements as a function of temperature and field proove the presence of a superconductive glass.The highest Tc sampels correlate with an orthorhombic-tetragonal structural phase transition.

please check for the english,thanks

Alex

Date: 9 December 1986, 10:29:48 EST From: RGREENE at YKTVMZ To: GGRIN

Let's stick to our Weds tennis.....4;30 right?

Rick

Date: 9 December 1986, 10:31:06 EST From: RGREENE at YKTVMZ To: POMERAN

Mel;

I can't take the court on Thurs. so why don't we just put off our game until next week.

Rick

Date: 9 December 1986, 10:37:27 EST From: RGREENE at YKTVMZ To: BED at ZURLVM1, KAM at ZURLVM1

Hi George , Alex;

Thanks for your note George. I will send you the Critical field data today. It seems to reproduce your low field results and has the data up to 7Tesla....I could go to 9T but will do that later. I assume from your note that you think that BLCO21 is still a single phase...is that correct? I will use this sample for the specific heat in a magnetic field.

I am a little puzzled by the critical field data...it suggests that your susceptibility data was measuring the superconductivity that occurs below 20K and the superconductivity above 20K may not be a bulk effect. It's also a litte disturbing that I measured such a large linear term in the specific heat in earth field.....the measurements at 5T should clarify this however.

Can you tell me the density of the SC phase? I need this to estimate gamma from the critical field slope. Also what is your estimate of the value of the resistivity just above Tc? I assume a single crystal would be at least 10 times lower. Also I would like to know your estimate of the Pauli susceptibility above Tc from your data....this will give another estimate of gamma.

Thanks for sending me your info and figures of the structure..I hope it arrives before next Tuesday.

Best regards,

Rick

Date: 9 December 1986, 11:32:57 EST From: RGREENE at YKTVMZ To: MALOZEM

I don't know Creuzet that well but he seems to have done some good work and seems to know what he's talking about. I'm not sure how independent, creative or hardworking he is. What would he be doing here? How closely working with an RSM? Who with?

Rick

Date: 9 December 1986, 14:34:51 EST From: RGREENE at YKTVMZ To: POMERAN

Mel;
OK for Monday. SEe you there unless you hear otherwise.

Rick

Date: 8 December 1986, 18:56:40 SET From: j.g.bednorz BED at ZURLVM1 To: RGREENE at YKTVMZ

Hi Rick Sorry that you had to wait for the answer since Thursday.I've been in Germany since Friday. In November I told you on the phone, that something happened to that sample BLCO21II which I measured again one month after the first resistivity run. The resistivity curve showed a peak at 34K and a shoulder occurring around 25K after a 60 percent drop. At that time I was also surprised about the magnetic field dependence in the low temperature part.The resistance was increased by fields between 0-0.4 Tesla but seemed to saturate at values above, whereas the field dependence of the peak at 34K was smaller. It would be good to compare our results, especially as you have the possibility to go to higher fields than 0.7 Tesla, which is the limit for our resistivi- ty system. Unfortunately I do not see the occurrence of a new phase related to the appearence of that shoulder in the resistivity.

Concerning your internal seminar, I will send you an X-ray powder spectrum and the structure of La2CuO4, which I've drawn already, using the information given in a German article. You can even have the viewgraphs. We should discuss questins about the structure at the phone.

Best regards
George.

Date: 9 December 1986, 18:47:08 SET From: j.g.bednorz BED at ZURLVM1 To: RGREENE at YKTVMZ

Hi Rick,

Thank you for your quick answer. I just discussed with our Japanese guest Masaaki Takashige, who is involved in the susceptibility measurements. First of all you should not be worried about about the susceptibility data shown in the preprint, because the samples shown there are not single phases. You will see from the X-ray pattern that the amount of the foreign phase can be very large,greater than in BLCO21 I. Single phase means, that in the X-ray diagrams we only can detect the La2CuO4:Ba. The small suscepti- bility could indicate that only parts of that phase is superconducting, for instance an intragranular network. That is the reason, why we think the density of La2CuO4 (from the X-ray data = 7 g/ccm) would not lead to a correct estimation in your case. The Pauli susceptibility

of sample BLCO21II, this sample is not shown in the paper, shows a field dependence close to Tc, this dependence is getting weaker with increasing temperature,and we expect it to vanish 10 or 20 de- grees higher, but in case of this sample it has not been confirmed. I'll give you values at 32-33K for the mass susceptibility:

0.3	Kgauss	1.28 E-7 ccm/g
5.0	"	1.35 E-6 ccm/g
10.0	"	1.61 E-6 ccm/g

Especially for the low field value we have to be aware of a large error.

For the resistivity value: My measurement (second one, where I realized the magnetic field dependence) showed a peak value of 7.36 E-3 Ohm cm.

Concerning the results of the Japanese group: Do you know more about it? How did they measure the 40% Meissner effect, did they measure ac or dc? Is something known about the magnetic field they applied? I think they believe the metallic perovkite phase is responsible for the superconductivity, whereas we found that the single phase samples containing La2CuO4:Ba in the powder diffraction pattern, show the highest susceptibilities. You will get the copies of the results as soon as they are plotted.

Best regards

George. can be very large, larger than in BLCO21.Talking about single phase samples

les,

Date: 10 December 1986, 10:48:47 EST From: RGREENE at YKTVMZ To: GRANT at ALMVMC

I haven't forgotten you....just busy as hell with this 30K superconductor and can't think about anything else. Happy Holidays Turkey.

Looks like I won't have time to ski...too much physics to do.

le Greene

GREENE
EXHIBIT C

Zurich Oxide 11|15|86 —

BLCO

DATA S(T,H)

RG

RG's writing

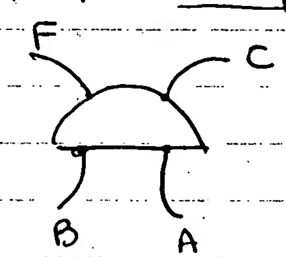
12/1/86

Resistivity of BLCO-21 II in Steve's He^3 Rig

Check out PAR first — usual diff input way $R_{Load} \approx 200k$

Using 100Ω R gives V = 1mV $\Rightarrow I = \frac{10^{-3}}{100\Omega} = 10^{-5}$ Amps $= 10\mu a$

Sample Setup



sample has non uniform thickness
In contacts – 1 mil Cu wires

At Room T

DC 2 probe

AB = 100Ω
AF = 88Ω
AC = 88Ω
BF = 72Ω
BC = 73Ω
FC = 62Ω

Do AC 4 probe (22 Hz)

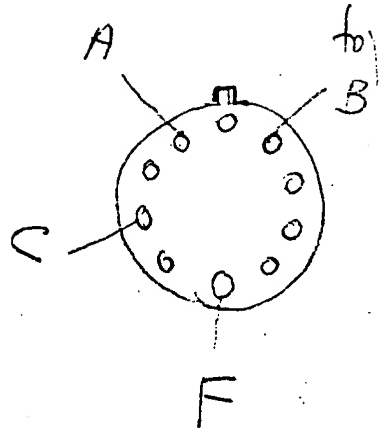
I = 10μa thru AB
get 12μV 90° out of R phase
⇒ 1.2Ω
I thru FC get 12μV on AB 90° out of phase
I thru FB get 12μV on AC " " "
I thru FA get 12μV on BC in phase

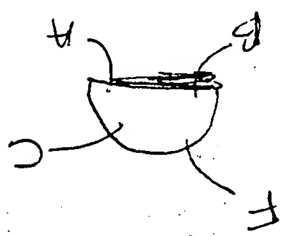
go to 5 Hz and get in phase signal
with ~ 80 mΩ resistance

Doesn't look good but let's try it any way
and use LR-400 bridge

DO NOT THROW AWAY

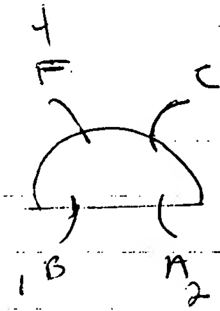
top view.





DC AB = 100
AF = 58
AC = 85
GF = 72
GC = 73
FC = 62

BFCO #21
Sample



At Room T – 4 probe

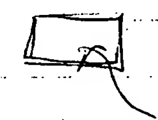
$R_{FC} = 75.6\ m\Omega$

$R_{AB} = 44.4\ m\Omega$

$R_{BF} = 7.4\ m\Omega$ ⟶ changes with excitation voltage + Ω scale

Cool down sample anyway using LR-400 AC Bridge to measure R_{FC} ($\nu = 16\ Hz$)

RuO2	T	R_{FC} (mΩ)
	300 K	76.0 mΩ
	cooling	R is dropping
	?	73.22
	?	70.00
	?	66.5
1059	?	63.7
"	—	60.45
1060		58.87
1061		57.36
1065		49.0
1074		46.0 ⟸ minimum
1057		49.0
		55.0
1260		0.4 mΩ ⟸ gets small
1340		0.32
1115		21.1 mΩ
1165		0.12 mΩ



1ma

$J = \frac{10^{-3}}{.2 \times .2}$

$= \frac{1}{4} \times 10^{-1}$

$= .025\ A/cm^2$

2 probe dc at 4K

FC = 99 Ω
AB = 158
AC = 147
AF = 142
BF = 118
BC = 115

Heat Sample pt by pt with H=0

RuO2	Ge	T	RFC (mΩ)	Comments
1240 Ω	650 Ω			
1336 Ω	1034 Ω	4.2 K	0.15 ±.01	0.06 Exit, .2 Range ⇒ I=300 nA
1326 Ω	885	4.8 K	0.15 ±.01	"
1306	779	5.5 K	0.15	"
1255	593	8 K	0.14	"
1203	490	11. K	0.14	
~~1174~~	~~361~~		~~0.18~~	
1172	430 ±2	13. K	0.14	Sorb at 18.0 K — 10x gain on RuO2
1153	303 ±1	17 K	0.74 ±.02	Still not regulating well at RuO2 = 1170 Ω takes ~ 5 minutes to come to equilibrium
1135 ±2	186 ±5		9.0 ±1	Does not regulate well here

May have too much gas in He^3 chamber — lower Sorb T

12/3/86

5

Run as f(H) at 4.2 K

2mv/amp { .0695 T/mV

Let's Run as f(T) again with H ≃ 0 — not quite zero because remanent field after H sweep remains

→ I = 300 μa

RuO_2 (Ω)	Ge-28387	T	R_{FC} (mΩ)	Comments
1155.5 ±.3	402 ± 1 Ω	~14.5	11.8 ± 0.1	Sorb at 10.9 - 0 mbar gas in SVC
1130	200 ± 20 Ω	~20 K	17.8	Not stable T's. only good to ± 20 Ω on Ge. Set sorb at 16 K 30 mbar He^3 pressure
1096	26 Ω	42 K	53.4	quasi equilib. - no heat sample cooling slowly from 42 K
1097	28.3		53.8	
1099	31.7		54.4	
1100	34.1		54.7	
1101	37.2		54.9	
1103	40.5		55.0	← this is maximum - starts to decrease
1104	45.0		54.6	
1105	48.0		53.9	
1107	55.0		50.4	cooling more rapidly now use set pt 1.1100
1110	65.0		39.0	
1112	—		30.0	← not good equilib.
1120	113		19.5	
1119	100 ±3		20.0	← trying to stabilize with set pt 1.1200 not so good
1126	150		15.0	
1130	175		10.7	
1132	181		9.4	
1138			5.0	
1141.7	256 ± 3		3.0 ± 0.2	Wait 20 Min for stable pt Set at 1140 - not that stable
1152 ± 1	330 ±3		0.45	quasi stable set pt 1150

Continue

RuO_2 B	Ge	T	R_{FC}	Comments
$1177_5 \pm 0.5$	$469 \pm 1\Omega$	$\sim 12.5K$	0.14	~~[illegible]~~ stable

Put on H field now

He boiling off rather rapidly — because sorb at 16K
and gas in SVC

try this tomorrow with gas pumped out of SVC

Put sorb heater at 3K, He^3 $p \approx 0$

12/4/86

I = 300 μa

Run some more T's and H's

Set Pt	RuO_2 (Volts)	Ge (Ω)	T (K)	R_{FC} (mΩ)	Comments
1.140	1.142_3	306 ± 1	17.0	3.5_5	Sorb 12.4K – no obvious P of He^3
1.137	1.139_5	283 ± 1	17.5	10.5 ± .1	Very stable pt – settings 50/20/30 on lupt. Small remanent H field causes a problem here but T is very stable. Ran field between these two pts (see field run ①)
1.135	1.137_5	264 ± 1	18.0	11.9	
1.132	1.134_0	236	19.0	13.5	
1.128	1.131_2	209	19.8	14.73	
1.125	1.126_2	161	21.8	17.0	By slowly increasing set pt we get very stable pts with this sorb setting
1.120	1.120_7	121	23.9	19.4	
1.112					
	1.112_7	76.5 ± 1	28.0	27.0	quasi equilib.
1.109	1.111	69.5	28.7	32.0	quasi stable

12/5/86

Some More — Sorb at 12.6K

T Reg. settings 50, 20, 30

I = 300 μa on LR-400
.06 Excita
.2V Range

RuO_2 (Volts)	Ge (Ω)	T (K)	R_{FC} (mΩ)	Comments
1.338		4.2K	0.15	
1.252_6	660 ± 1	6.7 K	0.15	Easy to equilibrate here
1.227_4	596 ± 1	7.7_5	0.15	
1.202_4	545	9.3	0.35	Is there still a small field from the Magnet? Yes
1.1774	492	11.5	~~2.13~~ → must be smaller	
1.162_5	439 8	13.3	5.30	reduces to ~ 1.0 mΩ by playing with field — keep field here and continue
1.152_7	385	15.0	3.0	
1.142_4	306	~~[illegible]~~ 17.0	~~[illegible]~~ 7.0 goes to 6.5 playing with field zero	~~[illegible]~~
1.131_5	209 ± 2	19.8	12.6 ± 0.3	
1.115_7	92 ± 1	26	22.5	
1.109_8	60 ± 1	30	43	hard to stabilize Sorb set at 15K

Try increasing current at various T's

Ge	T	R (mΩ)	I (from LR-400 setting)
526	10 K	1.65	300 ua
	"	1.8	30 ua
	"	1.9	1000 ua
	"	2.7	3 ma
		6	10 ma

but must worry about heating due to 200Ω contacts

T increasing

→ but RuO_2 T increasing

All this looks like increasing sample T via heating at contacts

Do this when we have better contacts

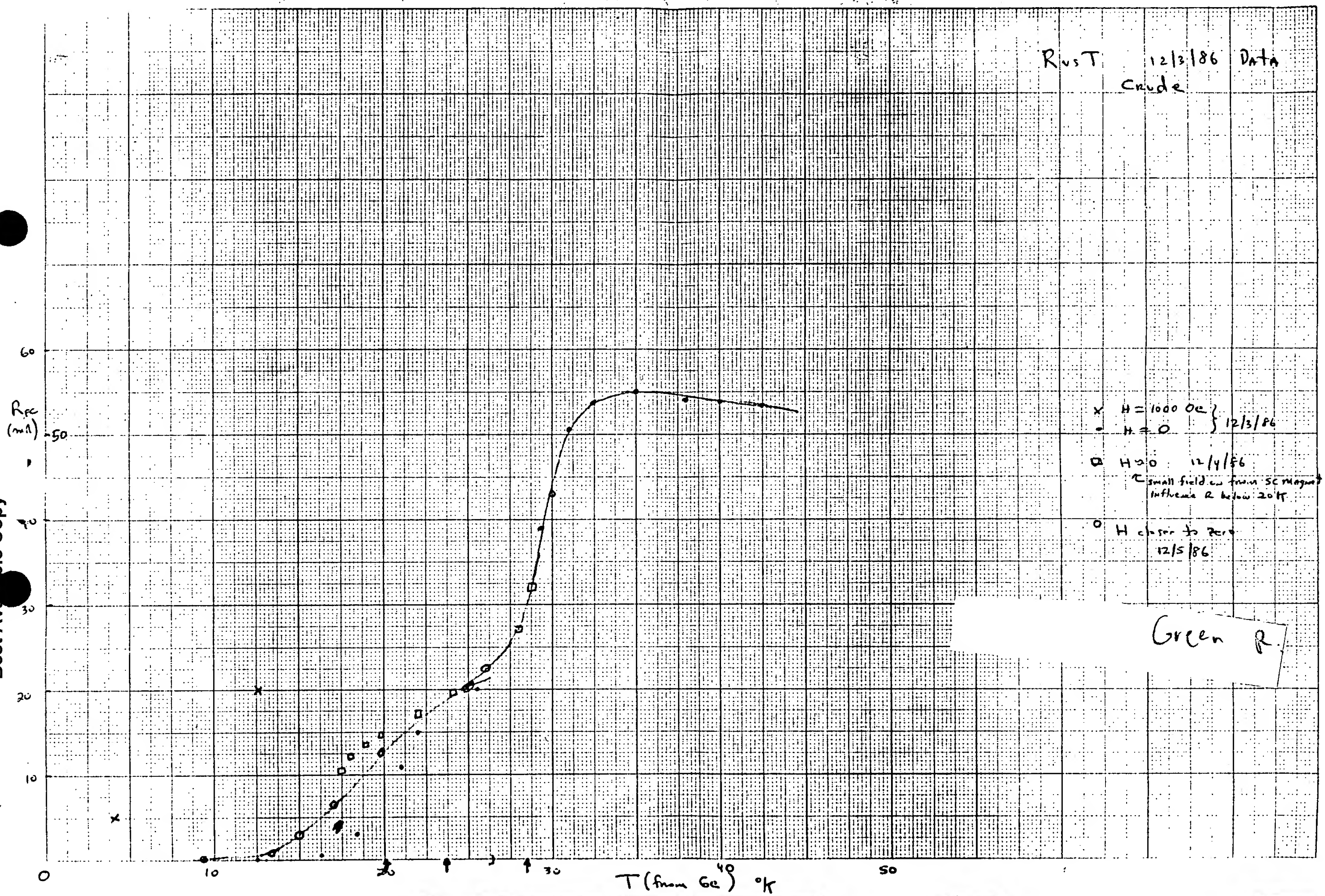
Estimate of Current Density

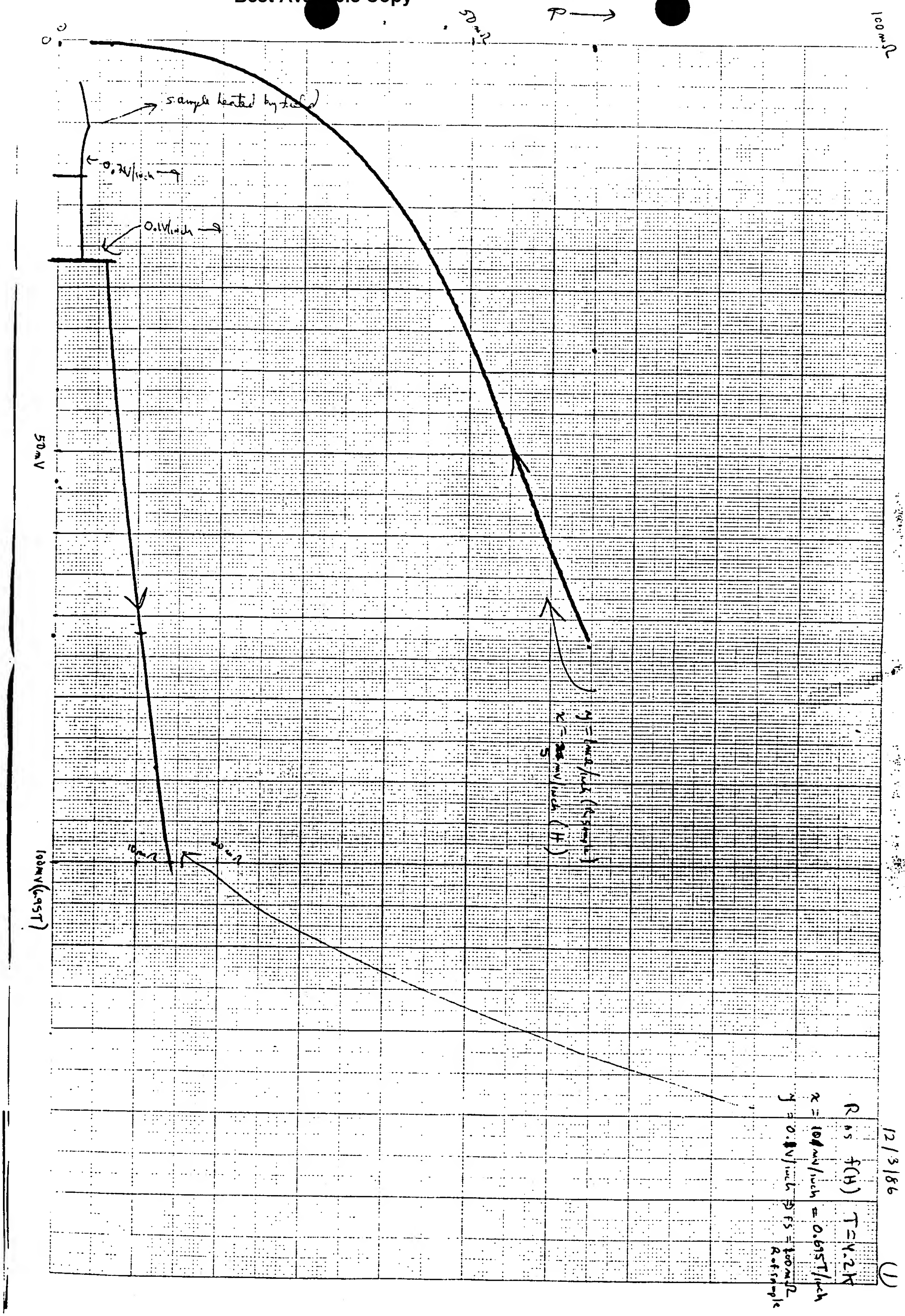
Cross section ~~2x~~ .25 m^2

$I = 300$ ua

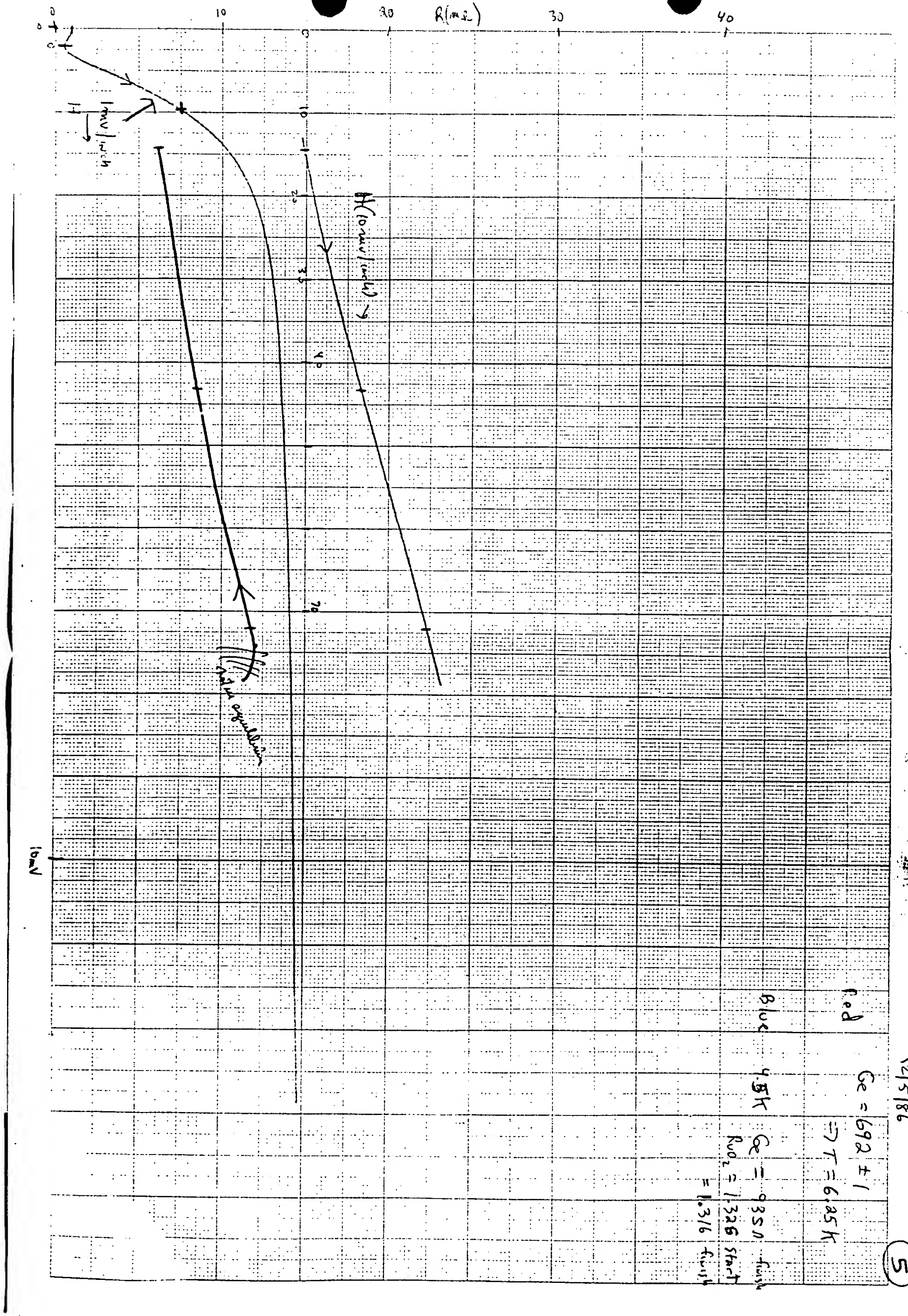
$$J = \frac{300 \times 10^{-6}}{.06} \simeq \frac{1}{2} \times 10^{-2} \; A/cm^2$$

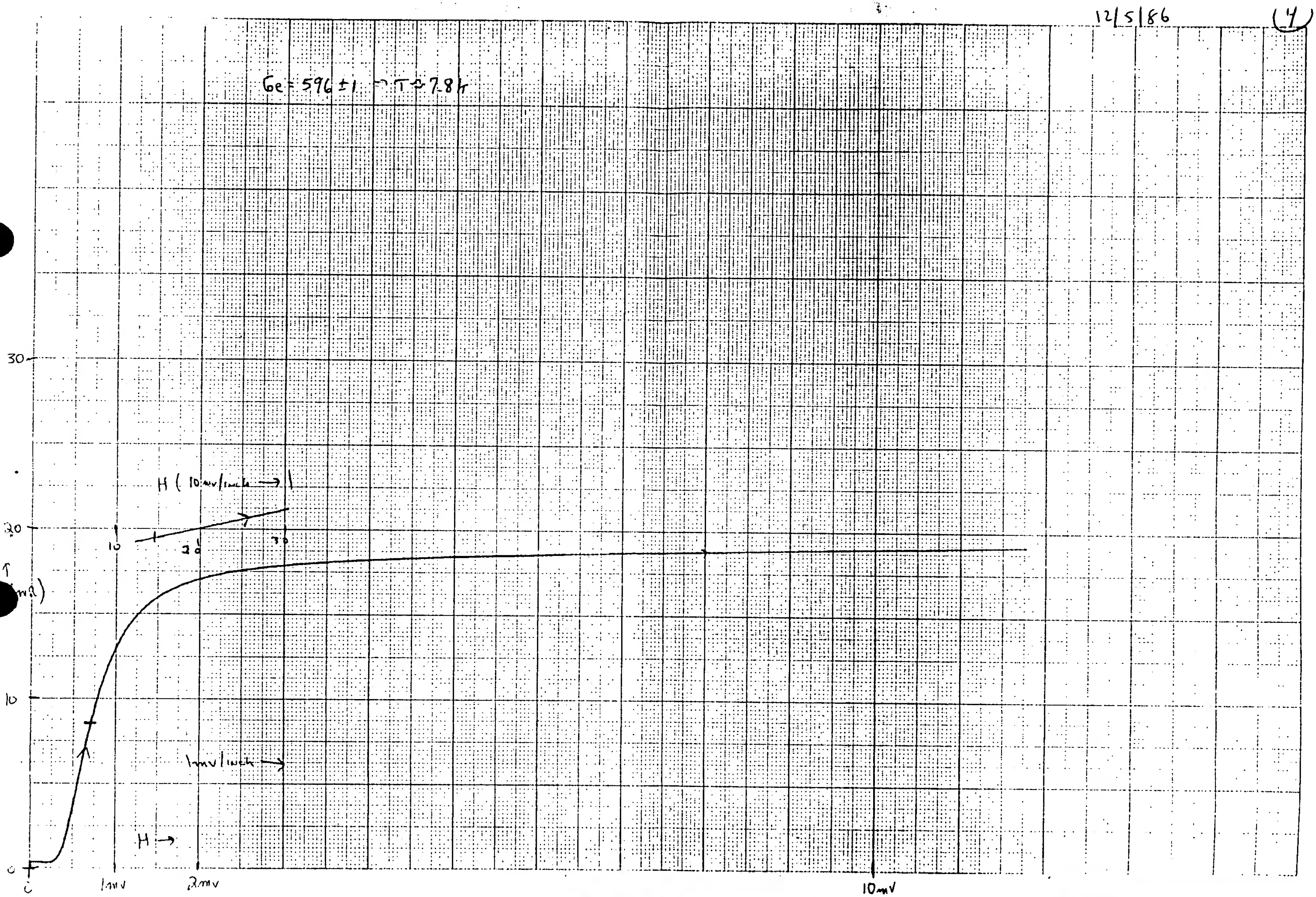
GREENE EXHIBIT D

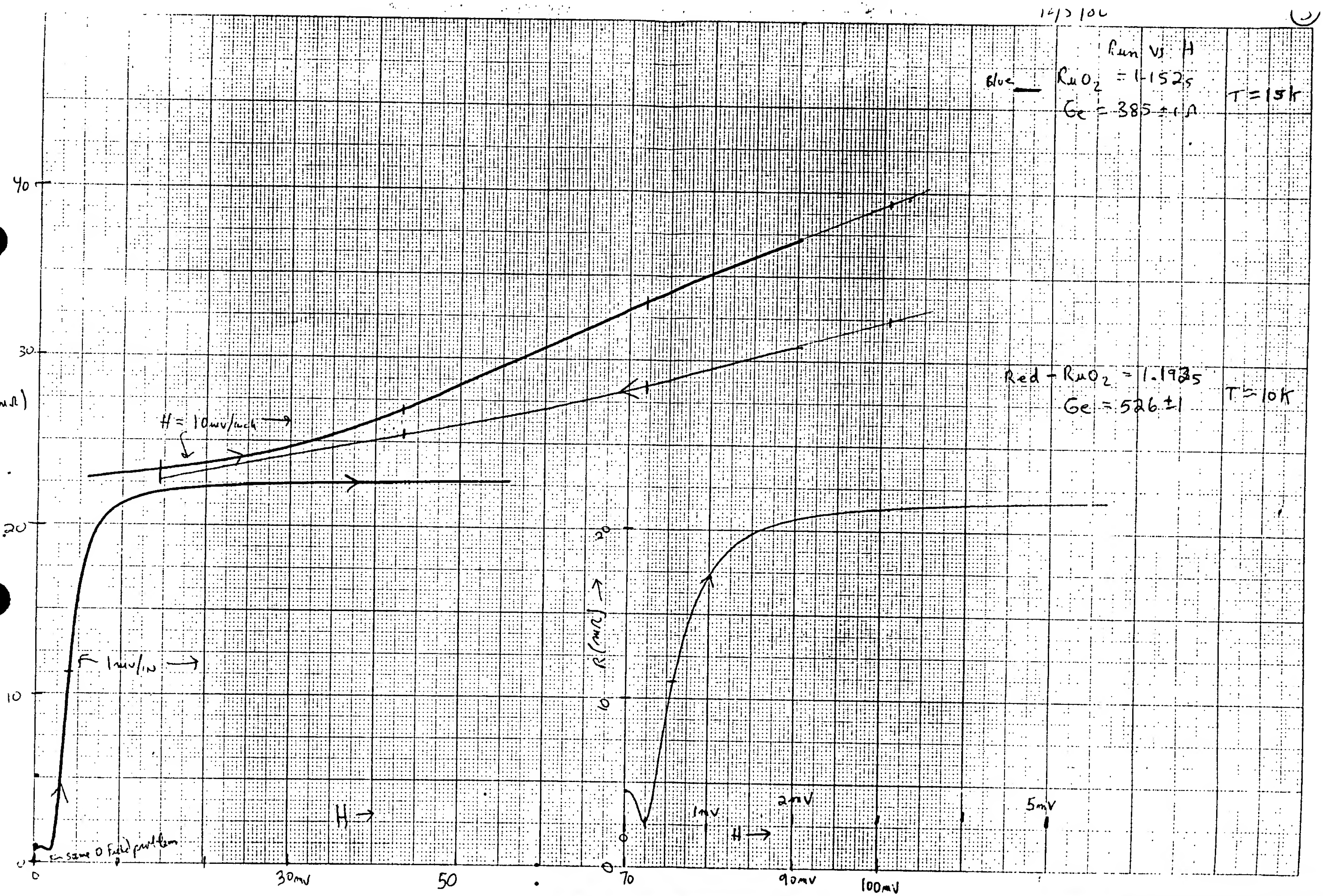


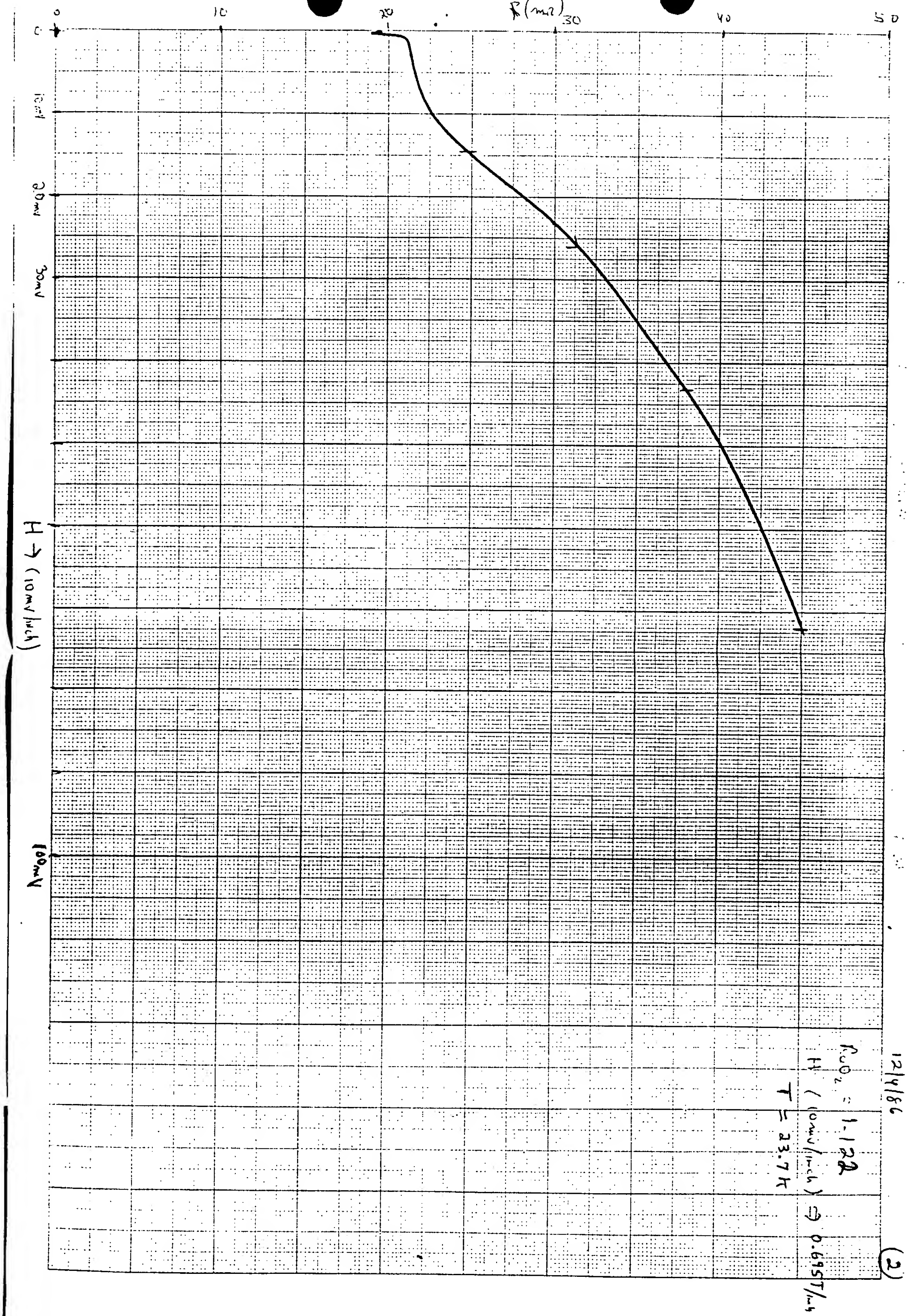


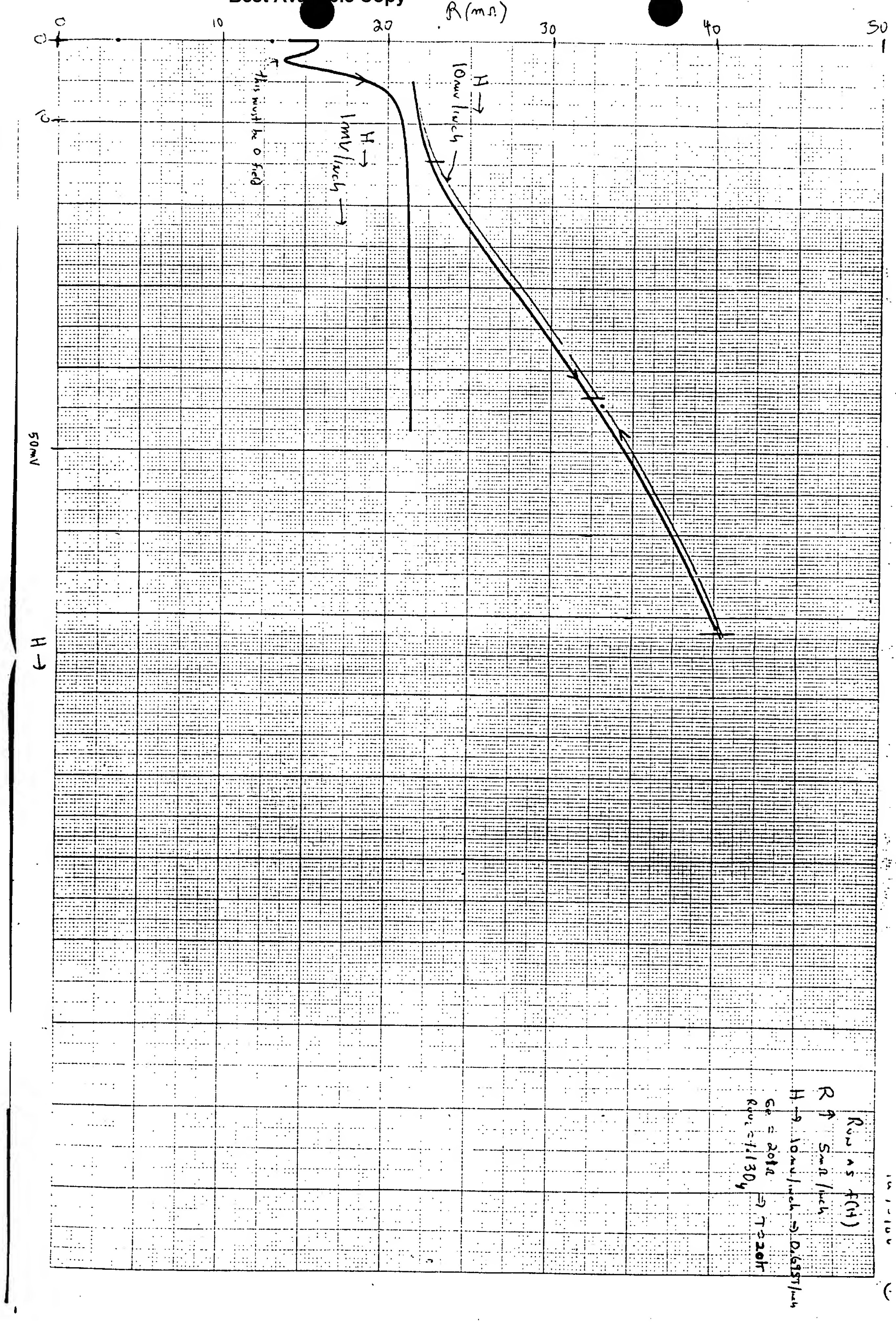
R →
50 mΩ
100 mΩ
sample heated by field
0.2V/inch
0.1V/inch
50mV
100mV (0.95T)
y = 1mΩ/inch (R sample)
x = 5mV/inch (H)
R as f(H) T=4.2K
x = 10mV/inch = 0.695T/inch
y = 0.1V/inch ⇒ FS = 100mΩ R of sample
12/3/86
1

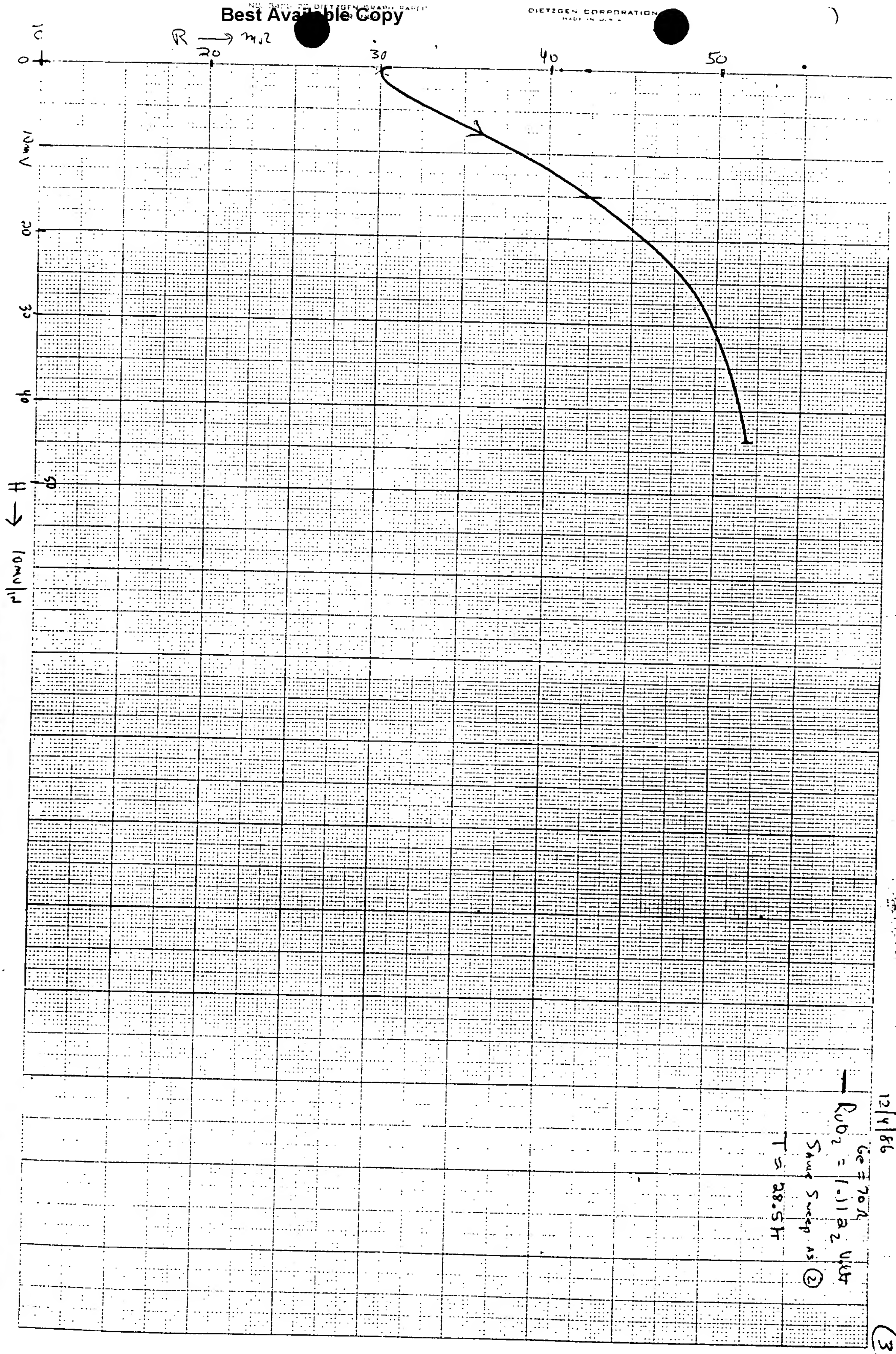

R(mΩ)
10
30
40
1mV/inch
10mV
ΔH(10mV/inch)
thermal equilibrium
Red
Blue
12/5/86
Ge = 692 ± 1
⇒ T = 6.25 K
4.5K Ge = 935Ω finish
RuO_2 = 1.326 start
= 1.316 finish
5

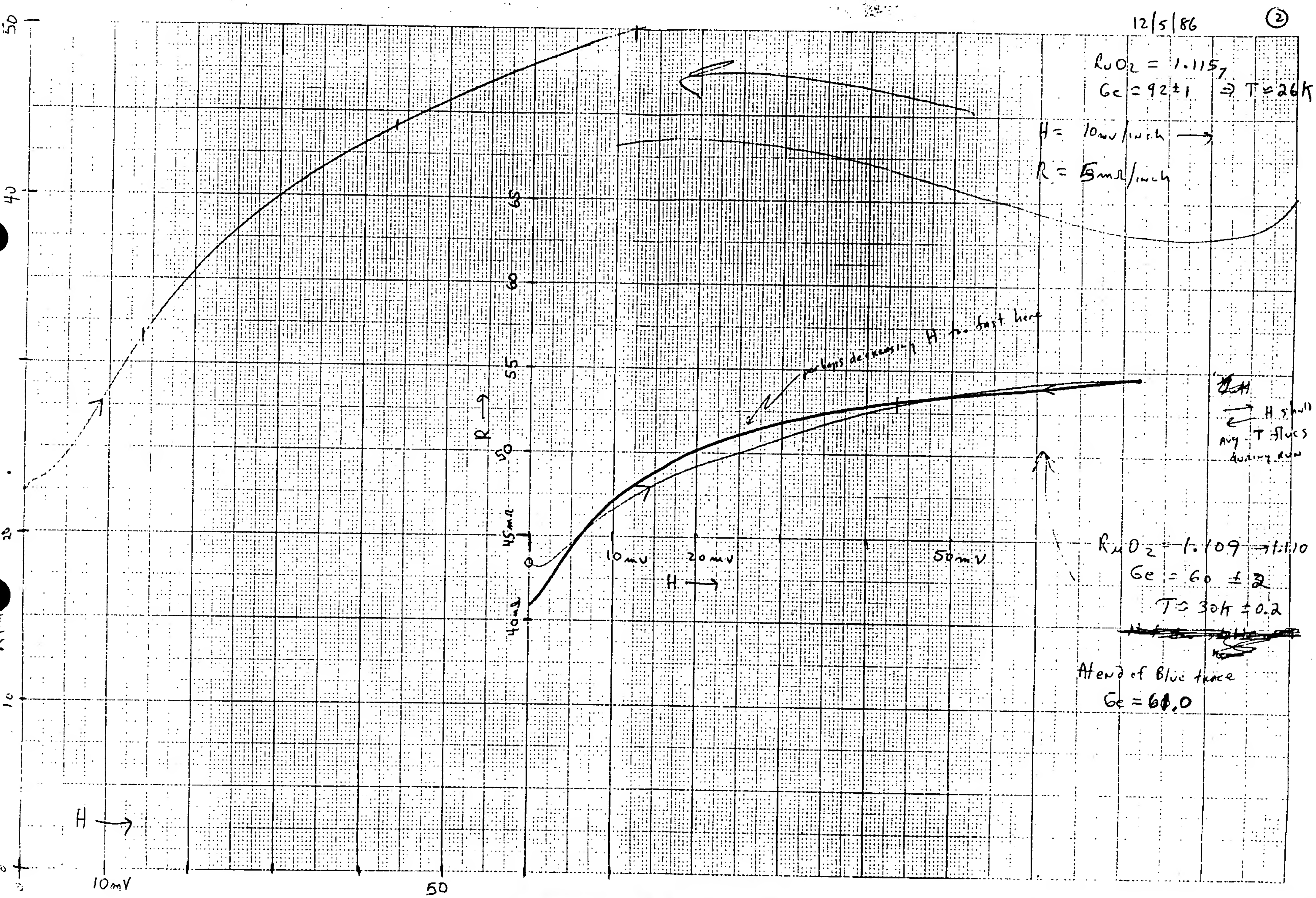

12/5/86
4
Ge = 596±1 → T≈7.8K
30
20
10
0
(mA)
H (10mV/inch →
10
20
30
1mV/inch →
H →
0
1mV
2mV
10mV

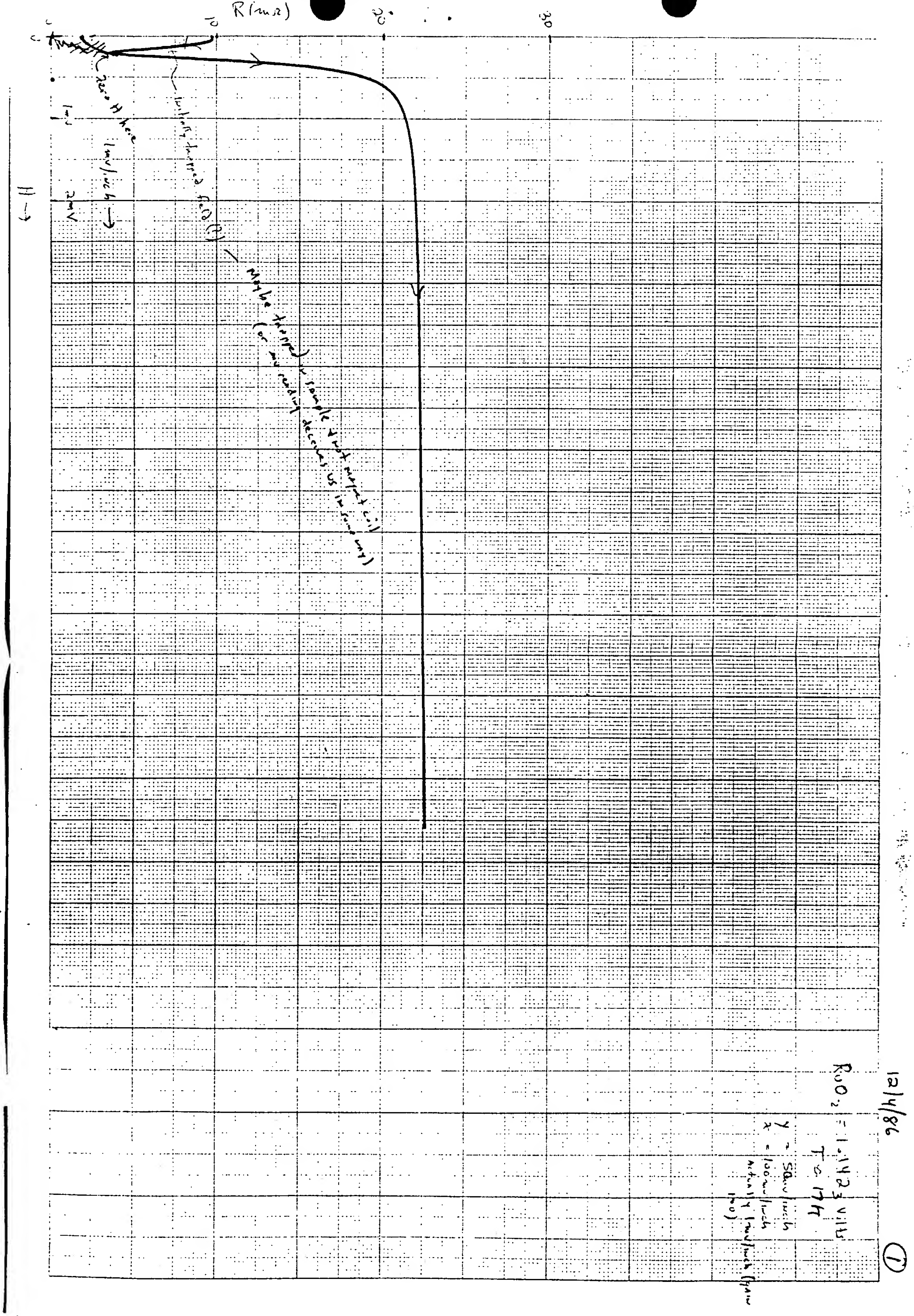

12/3/10
Run vs H
Blue — RuO2 = 1.152s
Ge = 385 ± 1 Ω
T = 15K
Red — RuO2 = 1.1935
Ge = 526 ± 1
T ≃ 10K
R(mΩ)
H = 10mV/inch →
F 1mV/in →
R(mΩ) →
H →
1mV
2mV
5mV
same 0 field problem
0
10
20
30
40
30mV
50
70
90mV
100mV


0
10
20
R (mΩ) 30
40
50
0
10mV
20mV
30mV
100mV
H → (10mV/inch)
12/4/86
R_{RuO_2} = 1.12 Ω
H (10mV/inch) ⇒ 0.695T/in
T ≃ 23.7K
2


R(mΩ)
0
10
20
30
40
50
H →
1mV/inch
H →
10mV/inch
this must be 0 field
50mV
← H
Rin as f(H)
R ↑ 5mΩ/inch
H → 10mV/inch ⇒ 0.695T/inch


DIETZGEN CORPORATION
MADE IN U.S.A.
R → mΩ
20
30
40
50
0
10 mV
20
30
40
H →
10 mV/1
12/4/86
Ge = 70 Ω
RuO2 = 1.11 a2 Volt
Same Sweep as (2)
T = 28.5 H
3


12/5/86
②
RuO_2 = 1.115₇
Ge = 92±1 ⇒ T = 26K
H = 10mv/inch
R = 5mΩ/inch
perhaps decreasing H too fast here
H shall
Avg T flucs during run
RuO_2 = 1.109 → 1.110
Ge = 60 ± 2
T ≈ 30K ± 0.2
At end of Blue trace
Ge = 60.0
R →
H →
10mV
20mV
50mV
40mΩ
45mΩ
50
55
60
65
10mV
50
10
20
40


R(mΩ)
0
10
20
30
H
zero H here
1 mV/inch
2 mV
initially trapped field (?)
Maybe trapped in sample & not magnet coil
(or mV reading decreases vs H in some way)
12/4/86
RuO_2 = 1.1423 volts
T ≈ 174
y = 50 mV/inch
x = 100 mV/inch
actually 1 mV/inch (gain 100)
1

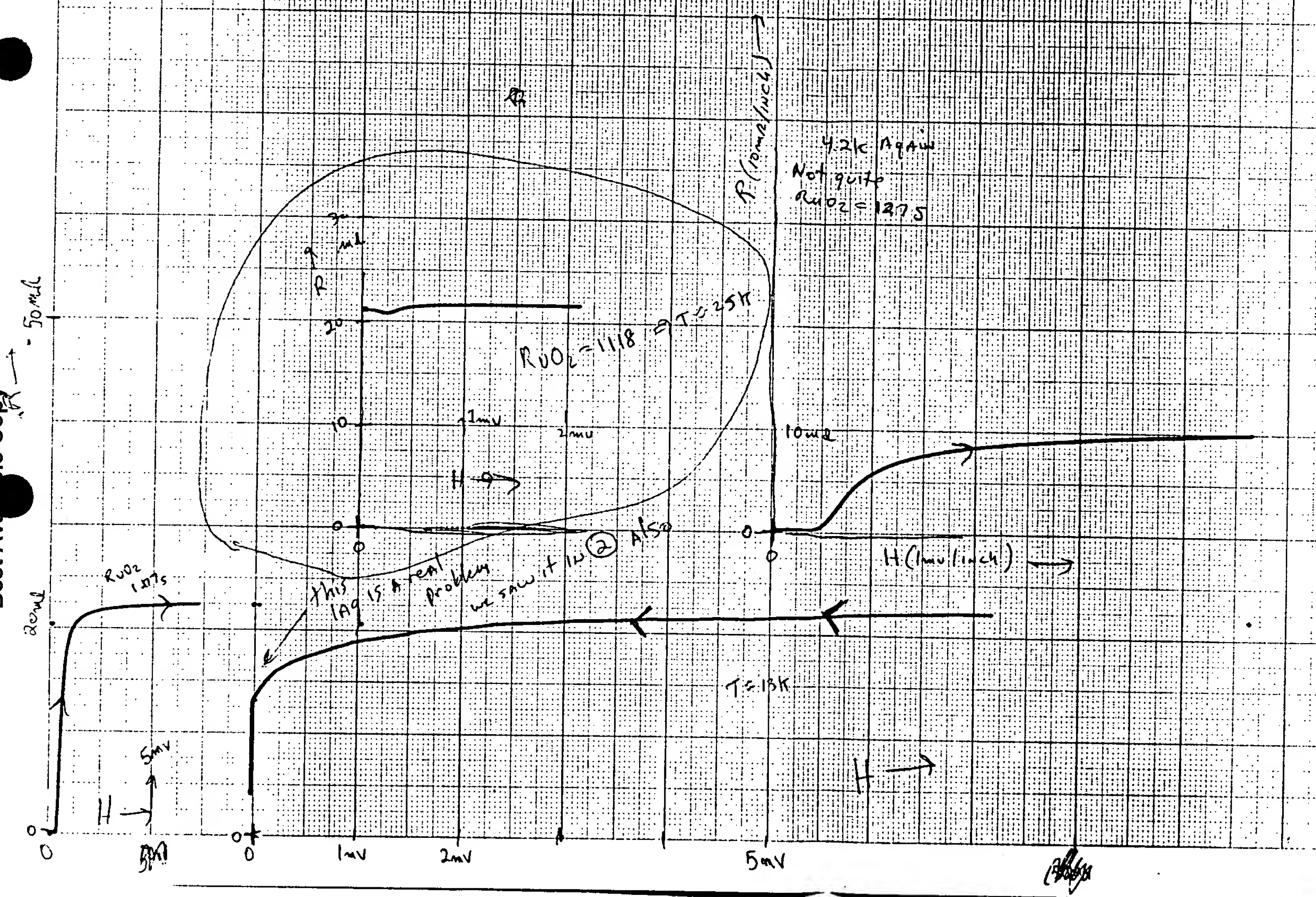
12/3/86 ③

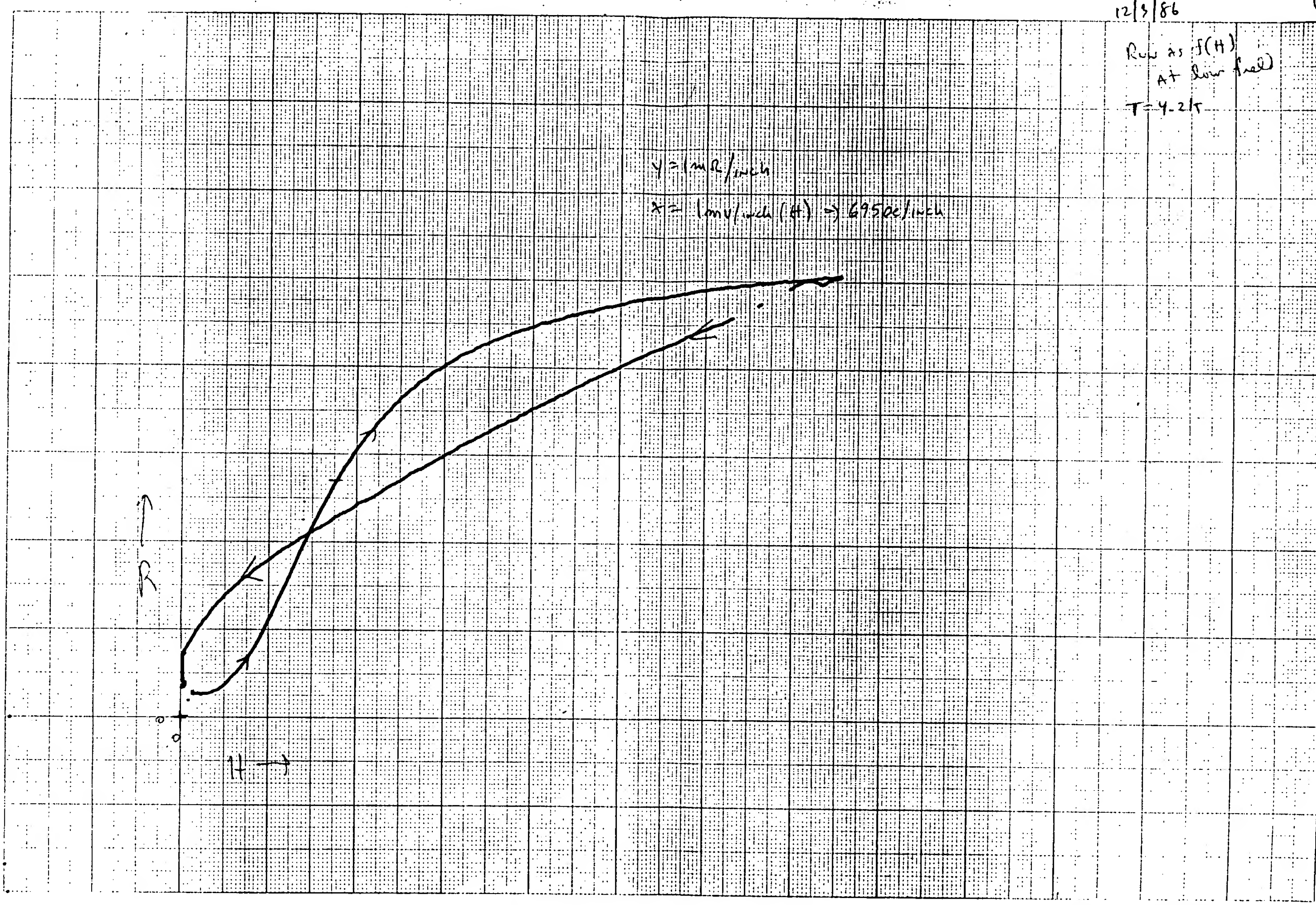
R as f(H) at T ≈ 13K

RuO_2 = 1.1775

y = 100mΩ FS

set at 1175




12/3/86
Run as f(H)
At low field
T = 4.2K
Y = 1mΩ/inch
X = 1mV/inch (H) → 695Oe/inch
R →
H →
0
0

NO. 340-20 DIETZGEN GRAPH PAPER
20 X 20 PER INCH

R. Greene – Torressen, et al

BaLaCuO 21II

12/8/86